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THE EFFECT OF DIFFERENT FACE STOCK MATERIALS ON MI- GRATION PROFILE OF PRINTING INKS

Master's Thesis

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ABSTRACT

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The aim of this thesis was to study the migration of the components of UV curing ink through different label face stock materials. Another goal was to find a correlation between the migration of components and permeability properties of materials. Three different critical components were scanned in the migration tests: photoinitiators, acrylate monomers and primary aromatic amines.

Samples consisted of polyethylene, polypropylene, polyethylene terephthalate and polyamide films of different thicknesses. The gas and grease permeability of the materials and the migration of ink components were tested and compared. The permeability tests for the materials consisted of water vapor, oxygen, carbon dioxide and olive oil transmission rate. The migration of ink components was studied using migration cells for sample preparation. Iso-octane, ethanol 95% and acetic acid 3% were used as simulants. Gas and liquid chromatography-mass spectrometry were used to single out individual migrants and the total amount migrated.

The migrated components consisted of photoinitiators and primary aromatic amines. Face stock materials most prone to migration were polyethylene and polypropylene. The photoinitiators detected in the chromatographic tests were: methyl-2-benzoylbenzoate, 4-phenylbenzophenone, 2-carboxybenzophenone, ethyl-4-dimethylaminobenzoate, 2-ethylhexyl-4-(dimethylamino)benzoate, 1-hydroxycyclohexylphenylketone, 2-methyl-4'-(methylthio)-2-morpholinopropiophenone, and 2,4-diethyl-9H-thioxanthen-9-one. Little to no migration occurred through polyethylene terephthalate and polyamide. The results indicate that a polyethylene terephthalate film with a thickness of at least 23 μm could act as a barrier for photoinitiator, acrylate and primary aromatic amine migration.

Physicochemical properties of photoinitiators can vary greatly. Substances have different polarity, lipophilicity and molecular mass. However, to a certain degree, the photoinitiator migration results have correlation with the permeability results. The non-polar gases of oxygen and carbon dioxide have similar behaviour as the non-polar or low polar photoinitiators with lipophilic nature. The results suggest that materials with high oxygen and carbon dioxide permeability are more prone to suffer from migration of non-polar lipophilic photoinitiators.

TIIVISTELMÄ

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Tämän diplomityön tavoite oli tutkia UV-kovettuvien painovärien komponenttien migraatiota erilaisten etikettipintamateriaalien läpi. Tavoitteena oli myös löytää korrelaatio komponenttien migraatiokäyttäytymisen ja materiaalien kaasunläpäisevyyden välillä. Tutkimuksen kohteena oli kolme eri painovärikomponenttia: fotoinitiaattorit, akrylaattimonomeerit ja primääriset aromaattiset amiinit.

Tutkimusnäytteet olivat polyeteeni-, polypropeeni-, polyetenitereftalaatti- ja polyamidikalvoja erisuuruisin paksuuksin. Polymeerikalvoista mitattiin kaasun- ja rasvanläpäisevyys, sekä painovärikomponenttien migraatio. Kaasunläpäisevyyksissä käytettiin vesihöyryä, happea ja hiilidioksidia. Näytteenvalmistus migraatiotutkimuksia varten tehtiin migraatiokennoilla. Simulanteiksi valittiin iso-oktaani, 95% etanoli ja 3% etikahappo. Kaasu- ja nestekromatografia-massaspektrometriaa käytettiin tutkimaan yksittäisten komponenttien migraatiota.

Fotoinitiaattorit ja primääriset aromaattiset amiinit migratoituivat polymeerikalvojen läpi. Migraatiota havaittiin pääosin polyeteeni- ja polypropeenikalvoissa. Kromatografisissa tutkimuksissa löydetty fotoinitiaattorit olivat: metyyli-2-bentsoylibentsoaatti, 4-fenylibentsofenoni, 2-karboksylibentsofenoni, etyyli-4-dimetyyliaminobentsoaatti, 2-etyyliheksyyli-4-(dimetyyliamino)bentsoaatti, 1-hydroksyyliisokloheksyyli-4-fenyliketoni, 2-metyyli-4'-(metyylitio)-2-morfolinopropiofenoni ja 2,4-dietyyli-9H-tioksanten-9-oni. Polyetenitereftalaatissa havaittiin lievää migraatiota ja polyamidissa ei lainkaan. Tulosten perustella voidaan todeta, että vähintään 23 µm paksuinen polyetenitereftalaatti toimii funktionaalisena barrierina fotoinitiaattoreille, akrylaateille ja primäärisille aromaattisille amiineille.

Fotoinitiaattoreiden fysiokemikaaliset ominaisuudet vaihtelevat suuresti. Yhdisteillä on tyypillisesti erilainen poolisuus, lipofiilisuus ja molekyyli massa. Voidaan kuitenkin todeta, että fotoinitiaattoreiden migraatiotuloksilla ja materiaalien hapen- ja hiilidioksidinläpäisevyydellä on yhteys. Poolittomien lipofiilisten fotoinitiaattoreiden migraatiokäyttäytyminen on samankaltainen poolittomien kaasujen diffuusion kanssa. Tulosten perusteella korkea kaasun- ja hiilidioksidinläpäisevyys merkitsee materiaalin olevan alttiimpia polaarittomien lipofiilisten fotoinitiaattoreiden migraatiolle.

PREFACE

Product safety and human health are the very foundation of this thesis. In the recent past, there have been incidents in which the migration of substances from printing inks has occurred through packaging materials. As a result of the migration is potential exposure to toxicologically hazardous chemicals. This thesis was made to evaluate the magnitude of printing ink component migration in label face stock materials.

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LIST OF SYMBOLS AND ABBREVIATIONS

CFIA	The Canadian Food Inspection Agency
CO ₂	carbon dioxide
CO ₂ TR	carbon dioxide transmission rate
DETX	2,4-diethyl-9H-thioxanthen-9-one
EC	European Commission
EDAB	ethyl-4-dimethylaminobenzoate
EHDAB	2-ethylhexyl-4-(dimethylamino)benzoate
EU	The European Union
FDA	The Food and Drug Administration
GMC	Grupo Mercado Comun
HDPE	high-density polyethylene
H ₂ O	water
JPIMA	The Japanese Printing Inks Manufacturers Association
ITX	isopropyl thioxanthone
LDPE	low-density polyethylene
MDPE	medium-density polyethylene
MTMP	2-methyl-4'-methylthio-2-morpholinopropriophenon
O ₂	oxygen gas
O ₂ TR	oxygen gas transmission rate
PA-6,6	polyamide 6,6
PAA	primary aromatic amine
PET	polyethylene terephthalate
PI	photoinitiator
PP	polypropylene
TiO ₂	titanium oxide
UV	ultra violet
WVTR	water vapor transmission rate
b	hole affinity constant
c	concentration
C _D	concentration gradient
C' _H	saturation level
D _D	concentration coefficient for Henry's law mode absorbed molecules
D _H	concentration coefficient for Langmuir mode absorbed molecules
D _{T1}	diffusion coefficient for Henry's law mode absorbed molecules
D _{T2}	diffusion coefficient for Langmuir mode absorbed molecules
ΔH _s	enthalpy change on dissolution
P	pressure
R	gas constant
S	solubility parameter
T	temperature
μ	chemical potential

1. INTRODUCTION

Migration safety is a trending topic in the packaging industry. Leaching of chemicals and components from the packaging material in direct contact with the packaged contents has been a growing concern for a longer period. In the field of pharmaceutical packaging the study of extractables and leachables has already been a standard procedure for a long time (Yu et al. 2017, p. 17). However, only during the last decade the packaging industry has started to also take into account the components not in direct contact with the contents, such as printing inks.

The first major scandal was in 2005, when isopropyl thioxanthone (ITX) was found in baby milk. ITX is used as a photoinitiator in ultraviolet (UV) curing printing inks. Low molecular weight of the substance makes it prone to migrate either by set-off or through the substrate. After the scandal, the whole packaging industry was alerted by the migration potential of substances from printing inks. In the case of 2005, ITX had migrated inside a reel from the printed surface onto the non-printed side of the substrate (Everts et al. 2009, p. 13). Another major incident with photoinitiators occurred in Germany 2009. Serious quantities of photoinitiators 4-methylbenzophenone and benzophenone were found in chocolate muesli. The muesli was packed in a cardboard box and separated from it using a polyethylene bag having no contact with the printed cardboard package. The substances were still able to transfer through the packaging to foodstuffs. These incidents made it globally relevant to start regulating the formulation of printing inks (EFSA 2009). However, even with these alarming occurrences, many countries and regions still have no strict legislation concerning printing inks.

Due to the growing interest in the component migration of printing inks and ensuring product safety, this Master's Thesis topic was given by UPM Raflatac. There are two goals for the thesis. The first one is to study the migration of UV curing printing ink components in different label face stock materials. The face stock materials are compared to see the impact of material selection on the migration behavior. The second goal is to compare the permeability properties of the materials, and search for a correlation between the permeability of a material and the migration of ink components. Also included in the theory section is a review of global printing ink legislations.

The analysis of the migration profile of the components consists of specific migration studies of photoinitiators, acrylate monomers, and primary aromatic amines. These are low molecular weight molecules with high risk of migration. Material permeability tests consist of water vapor, oxygen, carbon dioxide, and grease transmission rate tests.

2. REGULATIONS FOR PRINTING INKS IN PACKAGING

Legislation specifically addressing printing inks in packaging currently varies worldwide. Regulatory demands can range from nonexistent to strict continental agreements. The most comprehensive regulations are in the pharmaceutical and food industry, since the possible contamination of contents is a huge concern due to possible migration of components of the packaging.

2.1 Pharmaceutical packaging

In pharmaceutical packaging it is required to determine the extractables and leachables of the packaging material to ensure product safety. The testing is conducted in two parts (Everts 2009, p. 11).

The first step is determining the extractables. Extractables are chemicals which migrate from the packaging. The testing is conducted by simulating a worst-case scenario in which the material is exposed to solvents of varying polarity in elevated temperatures. The second step is to evaluate the possibility of contamination of the drug due to reactions with the migrants. This is a toxicological study, which involves the exposure of the migrants to the drug to assess the possible interaction (Yu et al. 2017, p. 17).

The quantity of extractables is currently not restricted by any concentration or volume limits. The study of extractables and leachables is only conducted to scan the possible toxicological substances. There are numerous different techniques and methods for testing which to a certain extent are based on official standards. However, pharmaceutical packaging must also pass food contact regulations which differ regionally (Jahn et al. 2010, p. 21-22).

2.2 Food-contact materials

Food packaging is also scanned for chemicals that could migrate into food. In the pharmaceutical industry the study of extractables and leachables is conducted using the pharmaceutical in contact with the packaging. However, in the food industry the packaging material is exposed to a simulant which mimics the impact of food contact. There are different simulants for fatty, acidic, aqueous and alcoholic foodstuffs (Arvanitoyannis et al. 2013, p 29).

Two different types of migration studies can be conducted. Overall migration testing is carried out in order to determine the total amount of substances migrated from the packaging. Another method is to scan the individual substances that have toxicological significance. Individual substances may have a specific migration limit depending on the regional legislation. Both tests are conducted under standard conditions. Incubation of the samples in food contact tests is much shorter than with pharmaceuticals, since the shelf-life is significantly lower (Arvanitoyannis et al. 2013, p. 29). However, regional legislations largely determine whether the package and its components are to be tested.

2.2.1 Europe

The European Union has multiple different regulations regarding food contact materials. Printing inks and their use is also included. The basis for all food contact regulations is Framework Regulation (EC) No 1935/2004 in which it is stated that the manufacturer of the final packaging is responsible for the compliance of the materials used. The transfer of harmful constituents from packaging to food is prohibited.

Printing inks and their use is regulated by the GMP Regulation (EC) No 2023/2006. This is commonly known as the Good Manufacturing Practice Regulation. General rules are introduced to all business operators in the supply chain demanding that proper quality assurance and control systems are established. Regarding printing inks, the regulation states that all printing inks used on the non-food side of the packaging should not migrate through the packaging or transfer due to set-off. This applies to manufacturing, packaging and the storing of the product. The printed side of the packaging should also not come in contact with the food unless proven safe for food contact.

A more specific regulation considering migration of substances is the Regulation (EU) No 10/2011. The regulation is for plastic materials and articles intended for food contact. As mentioned earlier there are two ways to assess the migration in food contact materials: overall migration and specific migration (Arvanitoyannis 2013, p. 29). Regulation 10/2011 sets an overall migration limit of 60 milligrams per one kilogram of food and individual substances are also limited by specific migration limits. Also included is a list of components which have been evaluated safe to use in food packaging. The list consists of monomers, additives and raw materials for plastics. Printing inks and their components also have to pass the specific migration and overall migration limits.

In addition to the regulations provided by European Union, the Council of Europe also has an influence on packaging of foodstuffs. While the Council does not issue laws or regulations, it provides the member countries with Resolutions. The member countries then partly use the Resolutions to model their own laws and regulations. Resolution AP(89) 1 lists impurities and potentially hazardous substances in mass colorants of plastics but the same principles apply to ink pigments as well. The Council also has issued Resolution AP(2005), which includes list of substances allowed for use in inks.

Countries also have their internal legislations and regulations. Switzerland has the Ordinance on Materials and Articles or SR 817.023.21, which consists of a positive list of toxicologically evaluated substances and their specific migration limits. Some substances on the list do not have a limit, but are still limited by the overall migration limit of 60 mg/kg. The regulation also includes a list of substances without toxicological evaluation which have a limit of 10 particles per billion.

In 2016, Germany issued a specific ink legislation. The German Ink Ordinance, or formally known as the Twenty-First Regulation amending the Consumer Goods Regulation, governs the formulation and application of printing inks used in food packaging. The use of substances, exclusion criteria and migration limits are included in the Ordinance with a positive list of chemicals used in inks such as monomers, binders, solvents and photoinitiators. It is possible to add chemicals to the list, but it requires a validation from the Federal Institute of Risk Assessment. Substances not on the list can still be used for ink formulations but must pass the migration limit of less than 10 particles per billion. The use of carcinogenic, mutagenic and reprotoxic chemicals is prohibited (EuPIA 2016, p. 1-4).

Nordic countries have a guideline in the form of publication Food Contact Materials and Articles: Printing Inks. It is not a law or strict regulation but rather a checklist regarding the use of printing inks for all parts of the package supply chain. The publication contains guidance for processing, equipment use, packaging material selection and ink formulation (Alsing Pedersen et al. 2012).

Even though multiple regulations have been set for printing inks in food packaging in Europe, there are four key requirements. All printed food packages must pass the criteria of Framework Regulation (EC) 1935/2004, GMP Regulation 2023/2006 and Regulation (EU) No 10/2011. Compliance with SR 817.023.21 is also required, since it is considered one of the most comprehensive regulations for printing inks in food packaging. (EuPIA 2014, p. 1-2)

2.2.2 North America

The United States regulations are governed by The Food and Drug Administration. There are no specific regulations for printing inks, but they fall under several other requirements. The FDA regulations are relatively more complex when compared to the strict European guidelines with specific lists and limits (Wagner 2013).

First of all, the FDA does not divide materials by their food contact compliance. However, the components of the packaging are listed as either direct or indirect food additives. Direct food additives are substances which are directly used in foodstuffs to perform a specific function or transfer to food due to set-off. These substances are allowed direct addi-

tion into food. Indirect food additives on the other hand are not to be added into food-stuffs. There is no intent for these substances to have any contact with the food, but due to possible migration may end up there (Wagner 2013).

Printing inks are potential indirect food additives. When the ink is on the non-food contact side of the packaging, it is only required that the converter of the package provides a sufficient barrier to prevent the migration. The barrier must separate the ink from food-stuffs. The FDA approves barriers such as resinous coatings, protective films or foils. With the barrier in place, the ink does not count as either direct or indirect food additive and must not pass the FDA guidelines. However, if the barrier fails to prevent the substances from migrating the ink will become an indirect food additive and must comply with the guidelines of 21 CFR parts 170-190. Migration tests may be required as a proof of no migration, but it is also possible to provide other data such as diffusion calculations. The FDA states that migration of less than 50 parts per billion can be ignored unless the substance is branded harmful (Wagner 2013).

Food packaging in Canada is regulated by the Canadian Food Inspection Agency (CFIA) and the Health Products and Food Branch of Health Canada. Regulations and standards are set by Health Canada and are then enforced by the CFIA. For food packaging the best practice recommended by Health Canada is to obtain a Letter of No Objection which states that the package is food compliant. The packer must provide detailed information about the printing ink, packaging process and migration tests to the Health Protection Branch of Health Canada. If it is possible for the packer to provide evidence that the printing ink is completely cured or there is a functional barrier in place, there is no need to test it for Letter of No Objection (Health Canada 2011).

2.2.3 Asia

Several countries in Asia have a wide range of food packaging regulations but some countries are still in the process of establishing their legislation. Some countries have very low demands for food packaging. Due to the geographically large size of the continent there are no unanimous regulations among countries.

China regulates food packaging according to Standard GB 9685-2008, Hygienic Standards for Uses of Additives in Food Containers and Packaging Materials. Printing inks have very similar regulations when compared to Europe. According to the Standard, migrating substances must not cause changes in foodstuffs, and their use should be as minimal as possible. Also included is a positive list of substances which are allocated to the scope of use, and in some cases to specific materials. There are substances listed specifically for printing ink formulations. Substances have specific migration limits similar to European regulations. A list of prohibited substances can also be found in the Annex A of the Standard.

At the moment the packaging laws of China do not comply in Hong Kong. The Food and Environmental Hygiene Department of Hong Kong and Customs and Excise Department are responsible for food packaging regulations. The Public Health and Municipal Services Ordinance (Cap. 132) states in Part V that all food sold must be fit for human consumption and all migration of packaging components which are hazardous to health is forbidden.

Food packaging regulations in Taiwan are stated in the Act Governing Food Safety and Sanitation. The requirements are that food utensils, food containers, packaging or food cleansers are not to be manufactured, sold, imported, exported or used if they are either toxic, cause unfavorable chemical reactions or are harmful to health. The Act also provides a list of migration limits for food contact materials. The list contains substances used in printing ink, but is not very comprehensive. A similar list is also used in the Philippines. However, it is regarded as a list of food additives, since their legislation states that all substances which are or may become in contact with food are food additives. Additives and the maximum amount allowed in foodstuffs is presented in Bureau Circular No. 2006-016.

Regulatory demands in Singapore are listed in the Sale of Food Act Chapter 283 section 56(1) in which the Part III section 37 sets standards for food packaging. The use of vinyl chloride monomer is restricted to 1 part per million and its migration to foodstuffs to 0,01 parts per million. The Act also states that the packaging must not contain or migrate carcinogenic, mutagenic, teratogenic or any other poisonous or injurious substances. Singapore's neighboring country Malaysia has similar regulations, but the migration of vinyl chloride monomer is restricted to 0,05 parts per million. Regulatory guidance in Malaysia is based on the Food Act 1983. More specifically Food Regulations 1985.

South Korean packaging standards are issued by the Ministry of Food and Drug Safety. All regulations regarding food packaging are stated in the Food Sanitation Act in which the Korea Standards and Specifications for Utensils, Containers and Packaging for Food Products takes into account the use of printing inks. Requirements are that the printing inks are not allowed to be in contact with foodstuffs. When applied on the non-food side of the packaging, migration of benzophenone must be less than 0,6 mg per one liter of food. The amount of residual toluene as an ink compound must not be more than 2mg/m² and the use of di-(2-ethylhexyl)phthalate in food packaging is forbidden.

Countries like Japan, India and Thailand only have voluntary regulations for printing inks, but no strict legislations. Thailand has the least demanding standards of these countries. Thai Industrial Standards Institute only has provided guidelines for the use of colorants in plastics, but the guideline includes substances which are also used in printing inks. The standard is called TISI 1069-2549 Colorants for plastics for food contact use. In Japan the Japanese Printing Inks Manufacturers Association or JPIMA has a list of substances that may be hazardous to human health. The substances on the list are forbidden to use in

formulation of printing inks. The list is called Voluntary Regulations Concerning Printing Inks, and is commonly known as the Negative List (JPIMA 2014).

The voluntary guideline in India is the Indian Standard 15495:2004 Printing Ink for Food Packaging – Code of Practice. It contains an exclusion list of substances for food packaging, and also guidelines for the use of printing inks in different types of packaging. According to the Standard, printing inks in secondary packaging can be formulated freely, but without substances from the exclusion list. Printing inks used in food contact materials must comply with the exclusion list, and not contain toxic substances. If the ink is in direct contact with foodstuffs it can only contain food additives.

2.2.4 Latin America

Mercosur is an economic and political union consisting of Argentina, Brazil, Paraguay, Uruguay and Venezuela. The union issues Grupo Mercado Comun Resolutions or GMC Resolutions, which are then included in the legislation of the member countries. GMC Framework Resolution 3/92 is the foundation for food contact regulations among Mercosur countries. In order for packaging materials to fulfill the requirements set in Resolution 3/92, they must be manufactured according to good manufacturing practices, and be of suitable purity. Migration of toxics, harmful compounds or substances which cause alterations in food is prohibited. Materials allowed in food contact applications are listed in a positive list. Migration is addressed in GMC Resolutions 56/92, 32/07 and 02/12 by setting overall and specific migration limits similar to Regulation (EU) No 10/2011. The migration test methods are included in GMC Resolution 32/99. These Resolutions indirectly set standards for printing inks, since the possible migration of ink components may not exceed the specific migration limits. Mercosur Resolutions have affected the Andean Community customs union, which has started developing their own legislation, but has yet to issue any regulations. The customs union consists of Bolivia, Columbia, Ecuador and Peru (Clark 2014, p. 5-6).

3. MASS TRANSPORT MECHANISMS

Mass transport in polymer films is a process which consists of several phases. The first phase is the adsorption of the diffusant on the surface of the film. Inside the film the molecules diffuse through the material. The process is driven by concentration gradients, but can also be affected by pressure and temperature. The final phase is the desorption of the diffusant, the opposite phenomenon of absorption (Feldman 2001, p. 50). The different phases of mass transport are presented in Figure 1.

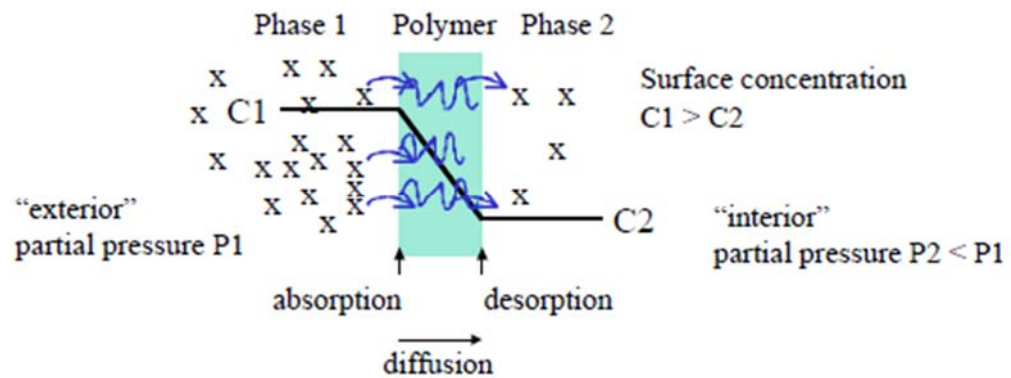


Figure 1. The phases of mass transport through a polymer film (Duncan et al. 2005, p. 7).

Small molecules migrate through the film materials due to the porosity of polymer matrix. Higher porosity results in more free volume in the matrix leaving room for small molecules to move in between the polymer chains. Free volume is dependent on the nature and physical stage of the polymer. All movement of molecules is governed by laws of thermodynamics (George et al. 2001, p. 997-999).

3.1 Adsorption

The first phase of molecular movement through polymer films is adsorption. Molecules of the diffusant dissolve in to the polymer matrix. Governing mechanism in adsorption is the occupation of free volume between the polymer chains (Carraher 2013, p. 495). However, there may also be other mechanisms involved in the sorption, which results in more complex mathematical models for diffusion. If it is not possible for the substance to dissolve into the matrix, due to for example large molecule size, mass transport cannot occur (Siracusa 2011, p. 2). If multiple different species are adsorbing into the polymer it is possible that they will compete over adsorption sites or even interact with each other (Duncan et al. 2005, p. 8).

Solubility of the molecule is determined by the enthalpy change on dissolution in the polymer matrix, and also the amount of free volume available. It is assumed that when the diffusant makes contact with the polymer, surface saturation level is instantly reached. This means that the mass uptake process begins immediately and thus the adsorption rate is determined by the rate at which it is possible for the molecules to diffuse into the polymer matrix. The adsorption will reach equilibrium state in a time determined by the dimensions of the polymer film and the diffusion behavior (Karimi 2011 p. 19-21).

Ideal adsorption of molecules into a polymer solid follows Henry's law:

$$C = SP \quad (1)$$

Concentration adsorbed C is directly proportional to the solubility parameter S and pressure P . However, solubility is affected by temperature T :

$$C = S_0 \exp\left(\frac{\Delta H_s}{RT}\right) \quad (2)$$

This means that the material solubility parameter is dependent on the enthalpy change on dissolution ΔH_s and the gas constant R (Duncan et al. 2005, p. 8).

Previous formulas only describe ideal adsorption behavior. However, many liquids do not follow the ideal model because the mass transport is governed by more than one adsorption mechanism. In two-mode models the dissolution of molecules consists of the ideal model governed by Henry's law, and also adsorption into micro voids and fillers in the polymer matrix, which is called Langmuir absorption (Duncan et al. 2005, p. 8-9; Suloff 2002, p. 22). When combining Henry's law and Langmuir absorption it is possible to predict the total concentration of the diffusants:

$$C = SP + C_H \quad (3)$$

The factor C_H describes the concentration adsorbed into the micro voids and fillers. It is dependent on the saturation level C'_H , hole affinity constant b , and pressure P :

$$C_H = \frac{C'_H b P}{1 + b P} \quad (4)$$

All in all the total concentration of diffusate molecules is:

$$C = SP + \frac{C'_H b P}{1 + b P} \quad (5)$$

It is important to notice that all polymers used in this study are semi-crystalline and in theory the crystalline parts of the polymer matrix are impermeable. This means that the solubility S is affected by the amorphous volume fraction (Suloff 2002 p. 50).

3.2 Diffusion

After the diffusate molecules have moved into the polymer matrix, a change in chemical potential and concentration is created. Relocation of diffusate molecules takes place due to random molecular motion, which attempts to remove the differences eventually resulting in a state of equilibrium. (George et al. 2001, p. 986-988) For a molecule there is no straight path inside the matrix of a semi-crystalline polymer, but the rate of diffusion can still be modeled since it is proportional to the concentration gradient of the diffusant (Aparacio et al. 2014, p.187-189).

Diffusion is governed by thermodynamic laws called Fick's laws (Vesely 2008, p. 303-304). The first law of Fick can be used to describe the flux of diffusant per unit area (J) through the polymer matrix as a function of the concentration gradient C_D :

$$J = -D_D \frac{\partial C_D}{\partial x} \quad (6)$$

In Equation 6, the concentration coefficient D_D depends on the concentration of the diffusant, but the equation only takes into account the molecules absorbed according to Henry's law, which means that C_D is only the concentration gradient resulted in by Henry's law diffusants (Suloff 2002, p.46-48). For systems in which the diffusants have absorbed into the matrix by two-mode mechanism, it is possible to model the situation using Fick's second law:

$$-\frac{\partial J}{\partial x} = -D_D \frac{\partial^2 C_D}{\partial x^2} = \frac{\partial}{\partial t} (C_D + C_H) \quad (7)$$

It was earlier suggested that the Langmuir mode absorbed molecules are immobilized and do not diffuse through the polymer matrix. However, since the concentration of the molecules and the chemical potential changes in the system, it is unlikely for the molecules to have no mobility. The chemical potential gradient can also act as the driving force for diffusion of two-mode absorbants instead of the concentration gradient (Suloff 2002, p. 46-47). The impact of chemical potential gradient can be mathematically modeled:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[\frac{1}{RT} (D_{T1} \cdot C_D + D_{T2} \cdot C_H) \right] \frac{\partial \mu}{\partial x} \quad (8)$$

In Equation 8, the diffusion coefficient for Henry's law mode absorbed molecules is D_{T1} while the diffusion coefficient for Langmuir mode absorbed molecules is D_{T2} . The chemical potential is μ and T represents the absolute temperature (Suloff 2002, p.47).

If the diffusion is occurring due to the concentration gradient it is possible to modify Equation 6 to also take into account the Langmuir absorbants. Henry's law and Langmuir species have their own individual concentration coefficients D_D and D_H and concentration gradients C_H and C_D . The equation is then changed to:

$$J = -D_D \frac{\partial C_D}{\partial x} - D_H \frac{\partial C_H}{\partial x} \quad (9)$$

Mathematical modeling of molecular diffusion in glassy polymers is very dependent on the diffusant. These equations can only be considered to generally explain the diffusion process and individual molecules may have different mechanisms for diffusion driven by other factors than concentration or chemical gradient (Vesely 2008, p. 303-304).

3.3 Desorption

Similarly to absorption, desorption is governed by Henry's law and it only occurs when it is thermodynamically possible. Desorption is always very likely to occur in situations where the concentration of the diffusant is higher inside the material than on the outside. Depending on the magnitude of the difference in concentration, the desorption rate can vary greatly (Carraher 2013, p. 495). Another factor is the affinity of the material for the absorbed species. A simple example is hydrophobic and hydrophilic materials, which either reject or absorb water (Duncan et al. 2005 p. 11).

4. FACTORS INFLUENCING MIGRATION OF MOLECULES

The mathematical equations presented in Chapter 3 are based on ideal diffusion behavior of a single substance. Polymeric materials used in commercial or industrial applications usually have different substances in their formulation including for example fillers, processing aids, antioxidants. Modeling diffusion in a multi-component system can be very complex and there are usually external factors, which have an impact on the mass transport process.

4.1 Polymer chemistry

The chemical composition of the polymer has a great impact on the diffusion properties of molecules. Compositional similarity between the polymer and diffusing substance result in higher solubility. For example, polar molecules will have a strong affinity for polymers with polar functional groups in their structure. Similarly when the polarity decreases so does the solubility (Duncan et al 2005, p. 11).

Chemical interactions between the diffusant and polymer are also possible. Depending on the magnitude of reactions, the polymer matrix may undergo structural transformations which result in changes in diffusion properties. Swelling, crazing, and partial dissolution of polymer matrix can be listed as few of these structural changes (Duncan et al. 2005, p. 11).

4.2 Free volume

The polymer chains which form the polymer matrix have microscopically small gaps between them. The combined volume of these gaps is called free volume. Depending on the alignment of the chains, the amount of free volume can vary greatly. The capacity for absorption and diffusion depends on the combined volume of the gaps. Polymer chains have mobility, which means that the dynamic movement can result in relocation of chains, which in turn opens up paths for molecules to transfer through (George et al. 2001, p. 988).

Chain mobility can decrease due to physical aging of the polymer. The temperature at which the polymer changes from glassy state to a rubbery state is called glass transition temperature. At temperatures above the glass transition temperature, the polymer chains are in a state of equilibrium, but when the temperature decreases chains have reduced mobility which means that the equilibrium state will be lost (Carraher 2013, p. 495).

However, even with the reduced mobility the chains will eventually move back to equilibrium, which means that the chains will not move from the equilibrium state once it is reached. This results in less possible paths for molecules to move inside the matrix (George et al. 2001, p. 988; Duncan et al 2005, p. 11-12).

Free volume decreases when the degree of crystallinity of the polymer rises. Crystallinity means that the chains in the polymer matrix are aligned in a certain order rather than randomly scattered. The amount of free volume is lower in crystalline parts, since the chains are packed in closer proximity to each other which also results in lower solubility and diffusion rate in these areas (Siracusa 2011, p. 7). Free volume between polymer chains is illustrated in Figure 2.

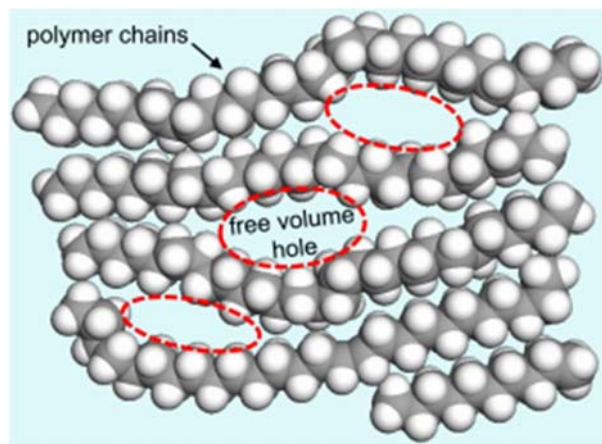


Figure 2. Free volume graphically depicted (Roilo 2017, p.2).

The alignment of chains can also be changed with different processing methods, such as hot drawing or extrusion. This is called orientation of the polymer chains. In semi-crystalline polymers the orientation results in reduced free volume due to enhanced crystallization. Orientation of amorphous polymers on the other hand results in directional dependence of chain mobility. The free volume gaps elongate to the direction of orientation, so that the molecules will have a longer path in the direction of the orientation, but shorter in the transverse direction. This also leads to anisotropic nature of diffusion properties (Duncan et al. 2005, p. 12; Carraher 2013, p. 495).

4.3 Material defects

During the processing and manufacturing of polymers it is possible to form voids and pores into the matrix. They are material defects which, unlike free volume, are independent of polymer chain motion and are on a macroscopic scale. The defects can form due to, for example air being trapped inside the polymer matrix during processing, mechanical stress or chemical reactions. Mechanical stress also has a large impact on the volume fraction of the voids, since hydrostatic tensile stress tends to open voids while hydrostatic compressive stress closes them (Duncan et al 2005, p. 12).

Voids and pores are completely open paths for the diffusants to transfer along. In the case of liquids and vapors, it is possible for them to condense into material defects which increases the saturation level, thus resulting in increased uptake. Higher porosity leads to increased movement of molecules through the polymer matrix. Pores can also be linked together which provides an even longer path for diffusants (Duncan et al. 2005, p. 12).

4.4 Fillers

Polymer materials used in industrial applications often contain filler particles and fibers. Fillers are used for modification of physical and processing properties. The modification of physical properties can consist of, for example reinforcing the polymer matrix, improving shrinkage control or even increasing the barrier properties (Anilkumar 2007, p. 18-20).

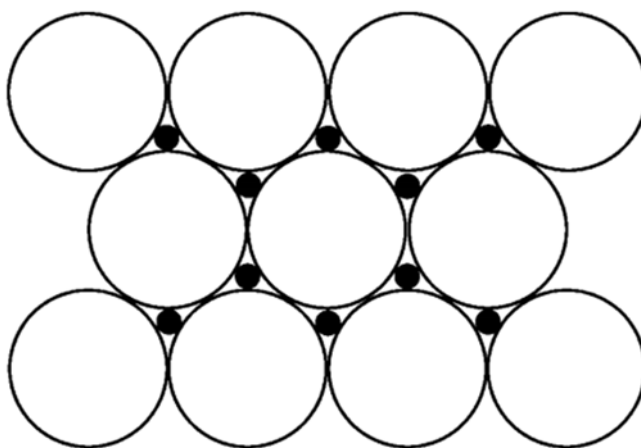


Figure 3. *Illustration of fillers inside a polymer matrix. Fillers depicted as black dots, polymer as white spheres (Rothon 2002, p. 10).*

Fillers can increase or decrease molecular movement in the polymer matrix. An example of fillers in a polymer matrix is depicted in Figure 3. Relative solubility of the molecule in the matrix and the filler governs the absorption behavior, if the solubility of the filler and matrix differ from each other. Commonly used inorganic filler particles such as glass, carbon, talc or silica are considered impermeable when compared to the polymer matrix, while organic fillers like rubber or natural fibers have higher solubilities than the polymer. The diffusion properties are influenced depending on the concentration of the filler in the matrix. For example, the higher the concentration of inorganic fillers, the greater the barrier properties are. The impermeable fillers block the transport path for molecules which then have to find a way around the particle leading to increased path lengths. As a result the mass transport rates are also reduced. Particle orientation is also a critical factor with longer particles, such as fibers. The diffusion behavior in the direction of the fibers may be very different when compared to the transverse direction (George et al. 2001, p. 994).

The interaction of diffusing molecules and the filler particles also has an impact on the diffusion properties. Higher surface energies of the filler and diffusant, when compared to the polymer, results in preferential absorption at the surfaces of the fillers. Strong surficial affinity of the fillers for diffusants leads to increased overall solubility in the polymer matrix. This feature is dependent on the surface area, which means that keeping the particle volume similar but reducing their size increases the amount of absorption sites (Duncan et al. 2005, p. 13-14).

4.5 Temperature

The mobility of polymer chains is dependent on the temperature. Higher temperatures result in increased mobility of the chains and thermal expansion, leading to a lower density and more free volume. An increase in free volume enhances the solubility of molecules. The vibrational energies of diffusing molecules also increase, meaning they also have increased mobility. However, the closer the temperature gets to polymer glass transition temperature, the higher the possibility for phase changes in the matrix are. As mentioned earlier, diffusion properties in rubbery and glassy state of the polymer differ greatly (George et al 2001, p. 994-995).

4.6 Presence of multiple diffusants

Diffusion and permeation properties of materials are performed exposing the material to only single chemical species under defined conditions. In industrial applications the materials are usually exposed to multiple different chemicals which greatly increases the number of possible diffusants. The migration properties can in theory change to any direction during the life cycle of a product. A diffusing substance may at first block sites to which other diffusants can no longer absorb, which leads to reduced solubility. On the other hand it is also possible that the first diffusant will cause swelling of the polymer matrix thus enhancing the solubility (Duncan et al. 2001, p. 18-19).

4.7 Physiochemical properties of diffusants

Physical properties of diffusants such as size, shape, phase and molecular weight have an impact on the movement of molecules. As the molecule size increases the diffusion coefficient decreases due to higher activation energy required for diffusion. In terms of the shape of the molecules, it has been found that flat or elongated molecules have higher diffusion coefficient than spherical molecules. Size and shape are more critical in glassy polymers since the paths for diffusion are more limited than in rubbery polymers (Anilkumar 2007, p. 17-18). Also the phase of the permeant has an impact on the mass transport process. Vapors and liquids tend to have much faster diffusion than gases, mainly because the saturation level is achieved faster when material is exposed to the diffusant (George et al. 2001, p. 994).

Molecular weight is the combined weight of all the atoms in a molecule. It influences the diffusion process to a certain degree. Lower molecular weight substances have a higher diffusion coefficient. In fact, the European Printing Ink Association lists all substances with molecular weight less than 1000 to be subjected for risk assessment due to their higher tendency for migration (Aparacio et al 2014, p. 189). However, it has also been stated that starting at a certain level the molecular weight no longer radically changes the diffusion coefficient, and thus the diffusion process is not affected (Anilkumar 2007, p. 13-14).

4.8 Stress and strain from external sources

During use polymers are subject to external mechanical stress and chemical exposure. Excluding internal, residual stresses, diffusion tests are usually conducted without any external influence, which means that this type of testing may not depict the actual diffusion behavior of a material in end use. Under tensile stress the permeability of a polymer material increases. As the strain increases microscopical cracks are formed which act as migration paths for molecules. At a certain point the increase in strain no longer has an impact on the mass transport, since the volume of the formed cracks is already so high. Chemical interaction combined with mechanical stress enhances the degradation of polymers which results in more rapid formation of cracks (Duncan et al. 2001 p. 16).

5. FACE STOCK MATERIALS

The materials included in migration studies are polymer films that are typically used for label face stock. The samples include polyolefin, polyester and polyamide films. The polyolefins used are polyethylene and polypropylene.

The polyethylene film samples are manufactured by blown film extrusion, and consist of medium-density polyethylene. Polyethylene films are not oriented after manufacturing, meaning that only the orientation from blowing process exists in the samples.

The used with polypropylene samples have gone through a modified version of blown film extrusion called the double-bubble technique. The process biaxially orientates the film. Only isotactic polypropylene was used in the samples.

Polyethylene terephthalate is used for the polyester film samples. The manufacturing method of the samples is cast film extrusion. The films are also biaxially oriented after the casting process. Cast film extrusion was also used for the manufacturing of the polyamide film samples, but only machine direction orientation is used in the manufacturing process. The raw material for polyamide films is polyamide 6,6. Polyamides are not the most common face stock materials, but are used in this study as a reference sample.

5.1 Polyethylene

Medium-density polyethylene (MDPE) is produced by heating ethylene under high pressure in the presence of a free radical initiator. MDPE has shorter and fewer branches than low-density polyethylene which results in a more crystalline structure. The crystallinity degree of MDPE ranges from 55 to 75%. Polyethylene is a non-polar polymer (Crawford et al. 2002, p. 23).

MDPE is flexible material which has a soft, wax-like feel. Its mechanical properties include high toughness and moderate tensile strength. It is slightly stiffer than LDPE. The density of MDPE ranges from 0,925 g/cm³ to 0,940 g/cm³. Higher density and crystallinity result in a more rigid material (Crawford et al. 2002, p. 23). The glass transition temperature of MDPE ranges from -80°C to -110°C and the melting temperature ranges from 120°C to 125°C (Martienssen et al. 2006, p. 484). Figure 4 presents the difference in chain branching in different polyethylene grades.

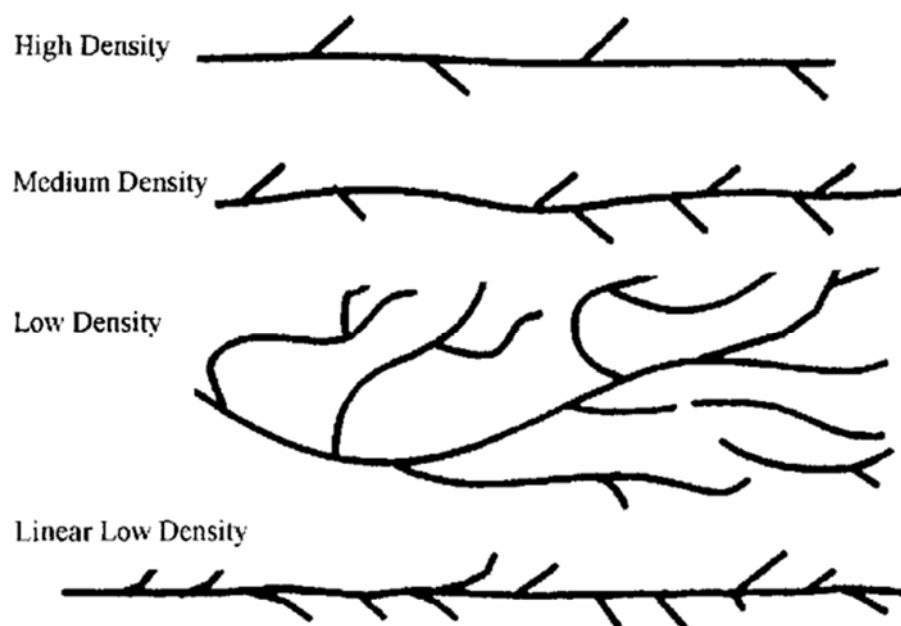


Figure 4. Presentation of the chain branching in different polyethylene grades (Hussin 2011, p. 10).

The chemical resistance is similar to LDPE and HDPE. MDPE has good resistance against acids, alcohols, alkalis, greases and oils but poor resistance against aliphatic, aromatic, and halogenated hydrocarbons, and also against esters, and ketones. Aromatic and chlorinated hydrocarbons will cause swelling of the polymer matrix of MDPE. Water absorption of polyethylene is very low, under 0,02% in 23°C for 24 hours. MDPE is affected by environmental stress cracking in the presence of polar liquids or vapors. It also has poor resistance against UV radiation (Wypych 2016, p. 351).

5.2 Polypropylene

Ziegler-Natta catalysts are used in high temperature and pressure to produce isotactic polypropylene (PP). Tacticity of polypropylene means that it has sterically ordered side groups, in this case all the methyl groups are located on the same side of the polymer chain. The isotactic nature of the polymer results in linear semi-crystalline structure. Polypropylene is a non-polar polymer (Venter 2015, p. 21).

Isotactic PP has high tensile strength and after orientation the mechanical properties enhance drastically. Biaxially oriented isotactic PP can have a crystallinity range of 40 to 70%. The toughness and hardness are higher when compared to MDPE resulting in a hard, waxy feel. The density of isotactic PP ranges from 0,90 to 0,91 g/cm³. Biaxially oriented PP has a melting point ranging from 148°C to 151°C and glass transition temperature of -10°C (Wypych 2016, p. 506-507). The relatively high glass transition tem-

perature means that for low temperature applications, it is required to blend other polymers like LDPE with PP in order to prevent the material from turning brittle (Shin et al. 2014, p. 252). An isotactic polypropylene polymer chain is presented in Figure 5.

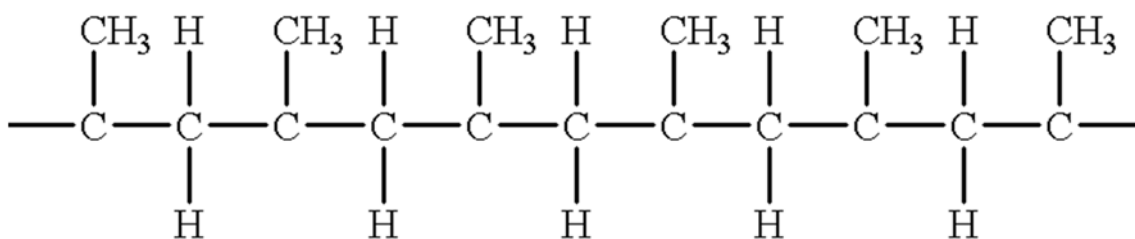


Figure 5. Isotactic polypropylene polymer chain (Venter 2015, p. 21).

Chemical resistance of isotactic PP is very good against acids, alcohols and alkalis. It is also resistant against greases, oils and ketones. However, resistance to aliphatic and aromatic hydrocarbons and also esters is poor, and results in the swelling of the polymer matrix (Emblem et al. 2012, p. 291). Isotactic PP also has a poor resistance to UV radiation. The water absorption of polypropylene ranges from 0,02% to 0,04% at 23°C for 24 hours (Wypych 2016, p. 508).

5.3 Polyethylene terephthalate

Polyethylene terephthalate (PET) is produced through polycondensation of purified terephthalic acid and ethylene glycol. PET is a semi-crystalline polymer with high degree of crystallinity. The small size of crystals results in a transparent polymer. The crystallinity of PET can be modified through orientation or heat treatment (Wypych 2016, p. 398-399). Figure 6 illustrates a PET monomer.

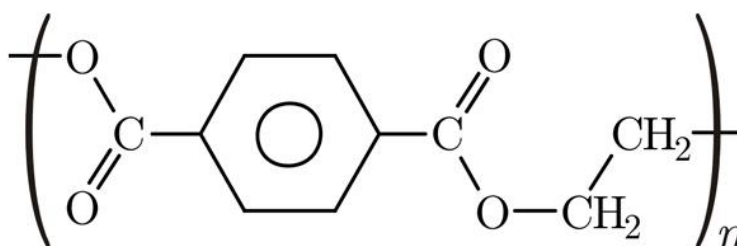


Figure 6. Polyethylene terephthalate monomer (El-Saftawy 2013, p. 49).

High crystallinity leads to high tensile strength, toughness, hardness and even stress crack resistance. The crystallinity in PET films can be as high as 85%. The surface of PET is smooth and surface quality is very good for printing. The density is much higher when compared to PE or PP ranging from 1,3 to 1,4 g/cm³. The melting temperature ranges

from 245 to 265°C and glass transition temperature ranges from 60 to 85°C. This means that at room temperature PET exhibits a brittle nature (Wypych 2016, p. 399).

Due to being a polar polymer PET possesses different chemical resistance than polyethylene or polypropylene. PET is fairly resistant against acids, alcohols, esters and ketones. However, offers good resistance against aliphatic hydrocarbons, aromatic hydrocarbons, greases and oils (Emblem et al. 2012, p. 291). Polarity also affects water absorption which ranges from 0,04% to 0,14% at 23°C for 24 hours. PET also has a very low resistance against UV radiation (Wypych 2016, p. 401).

5.4 Polyamide 6,6

Step-growth polymerization of adipic acid and hexamethylene diamine produces polyamide 6,6. The name comes from the number of carbon atoms the monomers possess. More commonly, polyamide is known as nylon (Shin et al. 2014, p. 254). Another name for polyamide 6,6 (PA-6,6) is poly(hexamethylene adipamide). PA-6,6 is a polar polymer with high crystallinity, which can range from 32% to 65 % (Wypych 2016, p. 221). The monomers and repeating unit of PA-6,6 is presented in Figure 7.

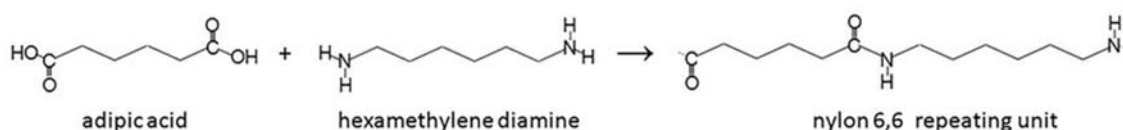


Figure 7. Monomers and repeating unit of PA-6,6 (Ortega et al. 2016, p. 2).

The density of PA-6,6 is in the range of 1,05 to 1,14 g/cm³. Key properties include high tensile strength, stiffness and high heat resistance. It has a glass transition temperature ranging from 56 to 70°C and melting temperature from 257 to 270°C (Wypych 2016, p. 222).

Similarly to PET, polarity results in higher water absorption which in PA-6,6, ranges from 8,5 to 9%. Such high water absorption can cause problems in converting and packaging applications. PA-6,6 has poor resistance against strong acids and both aromatic and halogenated hydrocarbons. On the other hand, PA-6,6 offers good resistance against alcohols, alkalis, aliphatic hydrocarbons, esters, greases, oils and ketones. Generally polyamides are known for their good chemical resistance making them a viable choice for barrier applications (Wypych 2016, p. 224).

6. UV FLEXOGRAPHY

Flexographic printing is one of the most used printing methods in narrow web applications, and the most common curing method is UV curing (Malcolm et al. 2005, p. 40). As mentioned earlier the aim of this thesis is to specifically address the migration of components from UV flexographic inks. Multiple substances in the ink formulation hold a migratory risk.

6.1 Flexographic printing

Flexography is a printing method used for printing onto foils, plastic films, corrugated board, paper, paperboard, cellophane and fabric. The process uses liquid inks which are typically dried using solvent or water evaporation and radiation curing. Drying and curing of the inks is a rapid process which results in fast printing speeds especially on non-absorbent materials such as films and foils (Oittinen et al. 1998, p. 135-137). An illustration of flexographic printing process is presented in Figure 8.

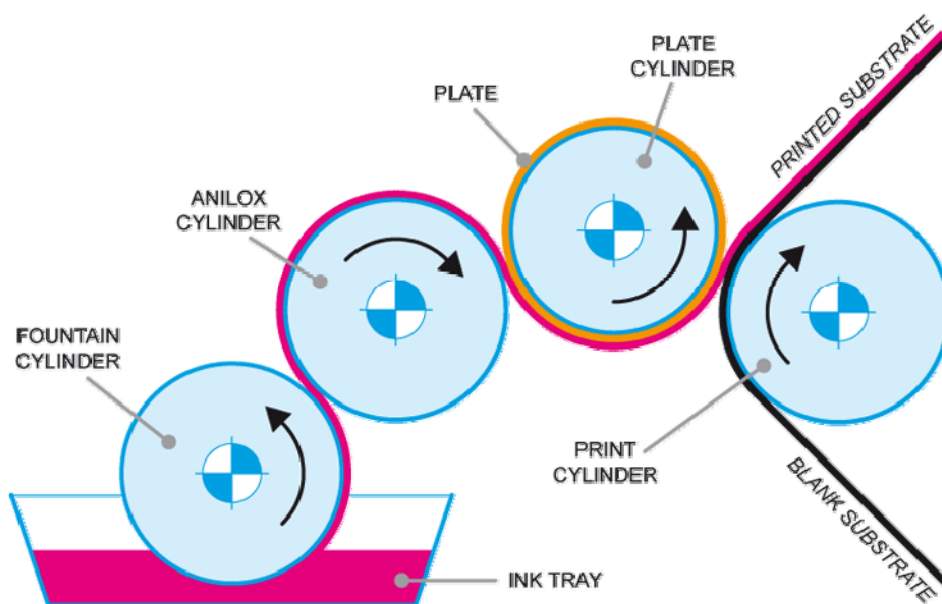


Figure 8. Illustration of flexographic printing process (ADHEPEL 2018).

The printing unit consist of an inking unit, a plate cylinder and an impression cylinder. The purpose of the inking unit is to transfer and meter a certain amount of ink onto the printing plate. Anilox roller and ink trough or tray are the main components of an inking unit. The anilox roller is either a ceramic or metallic cylinder with small engraved cells on the surface. The function of the cells is to pick up and move the ink onto the printing

plate (Leach et al. 1999, p. 36-37). The volume, number and shape of the cells varies depending on the desired print quality. The ink may be transferred to the anilox roller by using a roll, a fountain roller or an enclosed ink chamber system in which the anilox is in direct contact with the ink trough. Ink doctoring may also be used and typically in flexography this means using a doctor blade (Kipphan 2014, p. 397-400).

The printing plate is attached onto the plate cylinder which is in direct contact with the anilox roller. The printing plate is made out of soft flexible rubber or photopolymer. Similarly to letterpress printing, there are raised areas in the plate which pick up the ink from the anilox roller and press the image onto the substrate (Novaković et al. 2010, p. 403). The raised areas are called image areas and the lower parts of the plate are non-image areas. The substrate runs between the plate cylinder and impression cylinder which presses the web against the plate (Leach et al. 1999, p. 36-37).

6.2 Raw materials of UV inks

Basic formulations of ultraviolet curing inks are very similar to conventional inks which consist of pigment, vehicle, solvent and additives. The use of pigment depends on the end-use application and desired color. Primary aromatic amines are used to produce the color to the ink. These are very low molecular weight substances and thus possess a migration risk. Solvents are used to modify rheological properties of inks. These are typically low-viscosity monomers in UV-inks. The vehicle is the component which binds the pigment to the printed substrate after curing and consists of oligomers. Additives on the other hand are components which modify the physical and chemical properties of inks, and also consist of photoinitiators required for the initiation of curing reaction. A typical formulation of UV curing ink is 15-20% pigment, 20-35% oligomers, 10-25% monomers, 5-10% photoinitiators and 1-5% other additives (Leach et al. 1999, p. 641).

Oligomers are components similar to monomers but they are already polymerized to a certain degree, which results in higher viscosity of the ink. Monomers can be non-reactive or reactive. Reactive monomers form chemical bonds with the oligomers during curing which leads to formation of a uniform ink film. Acrylates are mainly used as oligomers due to their high reactivity, which ensures a fast cure rate. Three types of acrylate resins are the most commonly used in printing inks: epoxy acrylates, polyurethane acrylates and polyester acrylates (Glöckner 2008, p. 18-19).

Epoxy acrylates have high hardness, chemical resistance, high reactivity, high gloss and good adhesion. It is also an inexpensive component. However, due to having high hardness, epoxy resins lack flexibility after curing. Polyurethane acrylates on the other hand are tough, more flexible and have good chemical resistance. They can be divided into aliphatic and aromatic from which the aliphatic are a more expensive choice. Aliphatic polyurethane acrylates are more resistant to weathering than aromatic but are also less scratch resistant. Polyester acrylates have low viscosity which results in higher wetting

making it a viable choice for non-porous surface printing. Their chemical resistance is the lowest of all three acrylates (Glöckner 2008, p. 46-49).

Monomers are used as diluents which, unlike in conventional inks, bind with the pre-polymerized oligomers. These are called reactive monomers, and in UV flexography they are typically acrylates. However, there are not so many monomers to select from since many acrylates are toxic and volatile. Reactive monomers can be divided into monofunctional, difunctional, trifunctional and high functionality monomers. The functionality describes how many acrylate functional groups are present in the monomer structure. A higher number of functional groups leads to a higher chance of irritation in human skin contact which is why monofunctional acrylates are most commonly used. However, even though irritation risk is lower with monofunctional monomers, they are low molecular weight substances which means they pose a risk to migrate through the printed substrate if left uncured. There are also non-reactive monomers which plasticize the ink improving flow out and flexibility of the cured film. Typically used substances are high boiling esters, highly branched alcohols and alkyl phosphates. (Glöckner 2008, p. 48-50)

For UV curable inks, the key part in formulation is the photoinitiator which is required for the start of polymerization process after being exposed to UV radiation. Free radicals or cations form during energy absorption. The type of polymerization reaction depends on the photoinitiator (Izdebska et al. 2015, p. 191). There are three types of photoinitiators used in radiation curable inks, type I, II, and also cationic photoinitiators. Both type I and type II polymerization processes occur through free radicals, and as the name states, the cationic photoinitiators result in cationic polymerization (Lago et al. 2015, p. 2-4). There are multiple differences between free radical and cationic polymerization on the properties of inks. First of all the free polymerization reaction is not inhibited by humidity but it is inhibited by oxygen. The cationic polymerization has the opposite reaction towards humidity and oxygen. Full cure is achieved in a matter of seconds with free radical polymerization while cationic polymerization requires a longer time. This is partly due to the fact that UV radiation can reach deeper into ink matrix, but it's also because the chain formation in free radical polymerization is faster. However, ink film shrinkage and adhesion to the substrate is worse with free radical photoinitiators than it is with cationic (Glöckner 2008, p. 20-24).

6.3 Radiation curing

Both cationic and free radical polymerization techniques are used in UV printing inks. However, due to the longer cure time of cationic polymerization, free radical polymerization is a more common choice. In this study the UV ink used only contains free radical photoinitiators.

6.3.1 Free radical polymerization

Type I photoinitiators undergo a bond cleavage reaction when exposed to UV radiation. This is a unimolecular reaction meaning no other molecules are required for the formation of free radicals which are molecules with unpaired electrons. The homoclytic cleavage process initiates when the photoinitiator reaches the excited singlet or triplet state. Cleavage of bonds may occur at any weak bond, but it mostly takes place at the α -position of carbonyl group. The process is called α -cleavage. Another possible place for the cleavage is the β -position of carbonyl group which is the β -cleavage (Lago et al. 2015, p. 2). An example of different cleavage types can be found in Figure 9.

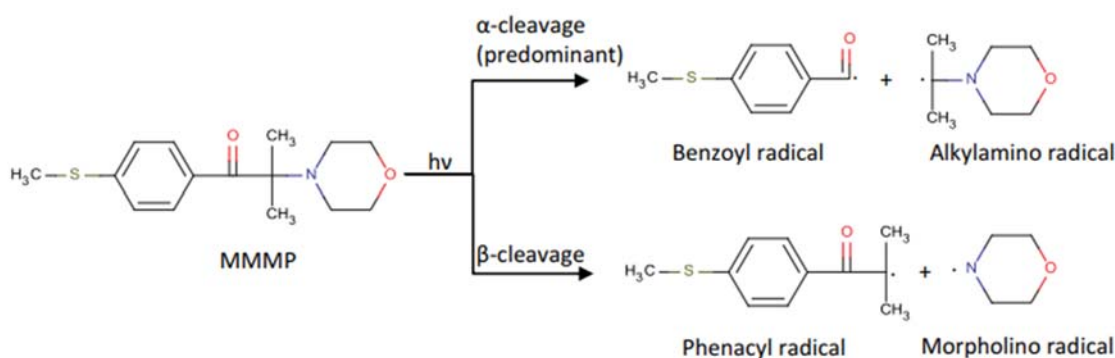


Figure 9. An example of α - and β -cleavage of type I photoinitiators. Photoinitiator depicted is methyl-4'-(methylthio)-2-morpholinopropiophenone (Lago et al. 2015, p. 3).

Unlike type I substances, type II photoinitiators cannot spontaneously produce free radicals in an excited state. The bond energies are too high for UV energy alone to cause any kind of cleavage reaction, therefore the use of co-initiator is required. There are two ways for co-initiators to produce free radicals: hydrogen abstraction from an H donor, the environment or through electron transfer from an electron donor (Coqueret 2016, p. 153).

The basic steps of free radical UV curing include initiation, chain propagation, chain transfer and termination. The initiation occurs when the photoinitiator is exposed to UV radiation, which causes the PI to enter an excited state. Type I photoinitiators are able to enter triplet state in which two free radicals are formed. Type II photoinitiators on the other hand enter singlet state from which they may enter the triplet state with the aid of a co-initiator. Molecules do not form free radicals in the singlet state. The free radical polymerization reaction is presented in Figure 10 (Lago et al 2015, p. 4).

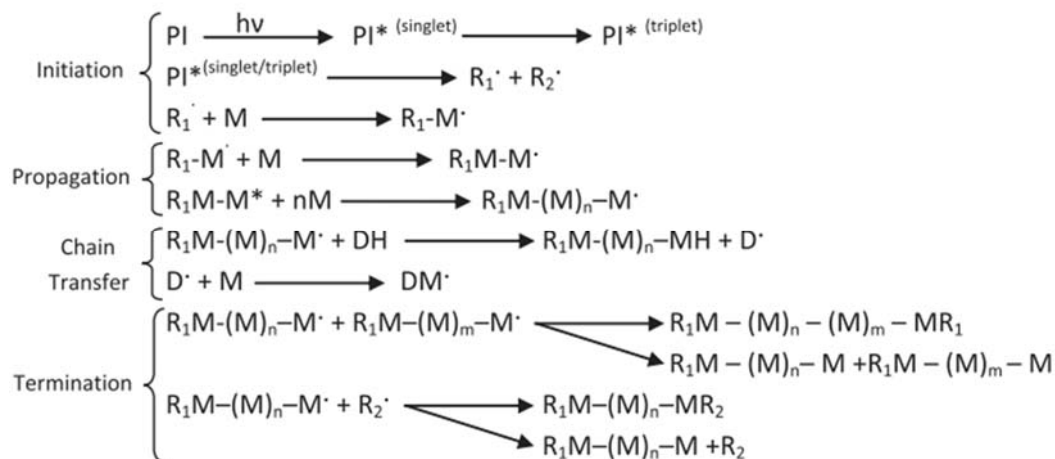


Figure 10. Basic steps of free radical UV photocuring. PI: photoinitiator, M: monomer, D: donor and R: free radical. (Lago et al. 2015, p. 2)

A free radical reacts with a monomer, which then has one excess electron resulting in the possibility for the monomer to react with another monomer. This is called the chain propagation step. The chain propagation reaction is assumed to be independent of the chain length. At any time it is possible for the forming chain to combine with another free radical instead of a monomer and result in an inactive molecule. This is a termination process via combination. Another possible way of termination is disproportionation which is also called the chain transfer which includes the abstraction of a hydrogen atom from a donor. Without the hydrogen atom the donor becomes a free radical, but is not able to start a chain propagation. (Lago et al. 2015, p. 2; Glöckner 2008, p 19-22)

6.3.2 Cationic polymerization

Cationic curing is technically a similar polymerization process as free radical polymerization since it is also a chain-growth reaction. However, the photoinitiators and chemical interactions are completely different. First of all the photoinitiator doesn't break into free radicals but rather is converted into strong acid species (Glöckner 2008, p. 22-23). Depending on the photoinitiator either Lewis or Brönsted acid is formed. Cationic photoinitiators are typically sulfonium or iodonium salts consisting of cationic and anionic pair. Upon exposure to UV radiation, the cationic part absorbs the UV radiation and the anionic part becomes the strong acid. Unlike free radical polymerization, the cationic polymerization process continues even after the photoinitiators are no longer exposed to UV radiation (Sangermano et al. 2014, p. 776-777). An example of cationic UV curing is depicted in Figure 11.

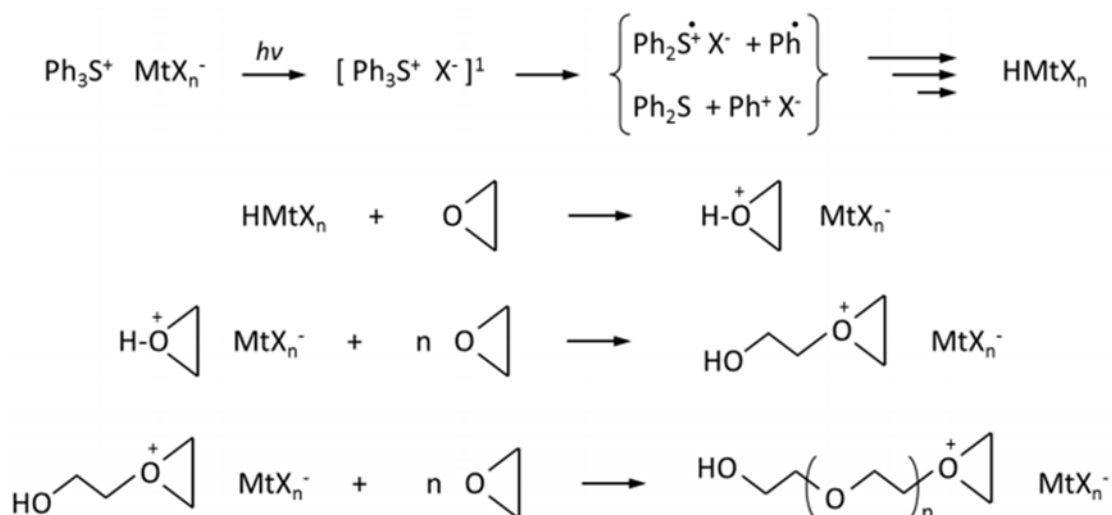


Figure 11. Simplified depiction of an epoxy monomer photopolymerization with a sulfonium salt acting as the photoinitiator. (Vitale et al. 2014, p. 556)

Instead of transferring a free radical along a forming polymer chain, cationic polymerization occurs by transferring a charge from monomer to monomer. Cationic curing starts with the heterocleavage of the photoinitiator. The photoinitiator enters an excited state under the effects of UV radiation resulting in the formation of anionic and cationic species. The cationic species react with a protonated monomer transferring the positive charge. The newly formed species then react with another protonated monomer propagating a chain. Termination occurs when the cationic proton is transferred from the polymer chain back to the photoinitiator. In theory, the chain propagation continues until all the monomers are consumed. However, factors like moisture and contaminants may act as chain transfer agents and stop the polymerization reaction. (Sangermano 2012, p. 2089-2091)

7. TESTING OF FILM BARRIER PROPERTIES

Barrier properties of films are practically crucial in pharmaceutical and food packaging applications. The testing of barrier properties can be conducted according to several different standards. This study includes the permeability testing of oxygen, carbon dioxide and water vapor. Grease resistance testing is also included.

7.1 Gas transmission rate

Key properties in packaging are water vapor, oxygen and carbon dioxide permeability. Permeability can be determined by the transmission rate of different gases. For example water vapor transmission rate (WVTR) describes the amount of permeating gas diffusing through the material during a fixed time period.

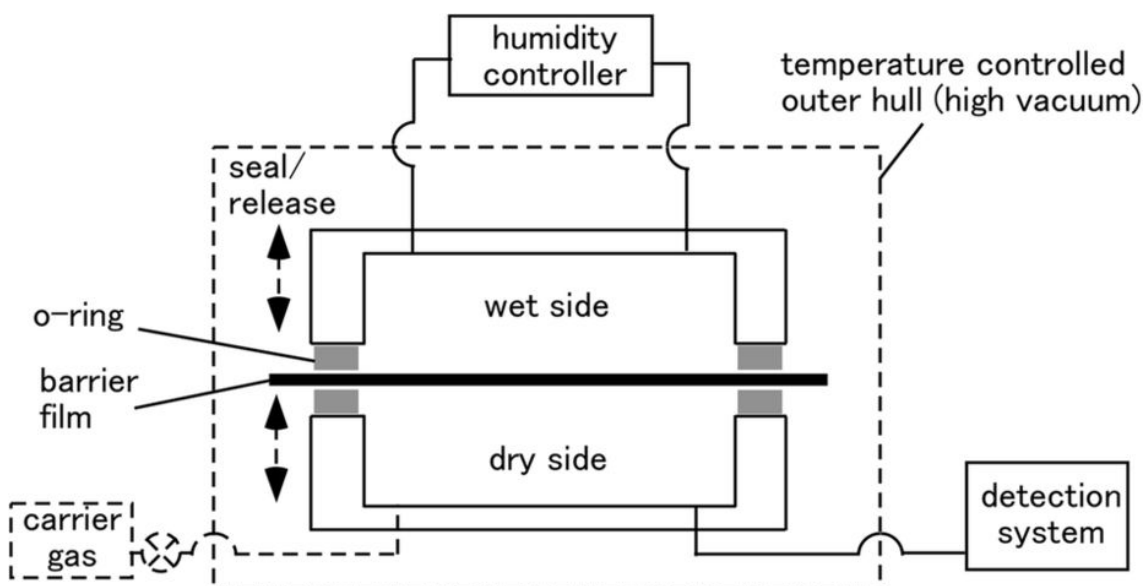


Figure 12. An exemplary setup of a WVTR test equipment. (Yoichiro et al. 2016, p. 2)

Permeability tests are conducted in a sealed chamber acting as a diffusion cell with two different sides which are separated from each other with the test sample. A typical test setup for WVTR is presented in Figure 12. Oxygen and carbon dioxide transmission rate tests are conducted with the same principle. (ASTM D3985-02 2002) On one side of the sample, there is a high concentration of the permeating gas, and on the other side the concentration of the permeant is zero. Carrier gas is conducted to the zero concentration side of the chamber. Before the test can begin the chamber must be heated to the desired level after which the temperature is kept constant. The high concentration side of the chamber is filled with permeant until a wanted pressure level is reached. Permeability

testing can be conducted with either equal or different pressure on both sides of the sample. The test gas diffuses through the film and mixes with the carrier gas which transfers the permeant to the sensors. The test ends as soon as the concentration of permeating gas is equal on both sides of the sample (Stevens et al. 2014, p. 1).

Typically three different types of sensors can be used: a U-tube with liquid inside, an infrared sensor, or a coulometric sensor (McKeen 2011, p. 13). The principle of U-tube sensors is that the carrier gas mixed with the permeant displaces liquid from the U-tube. The displaced volume is used to calculate the permeation rate. Infrared sensors measure the fractions of infrared energy absorbed by the permeant resulting in an electrical signal. The amplitude of the electrical signal can be analyzed to calculate the concentration of water vapor in the dry chamber, from which it is possible to calculate the permeation rate. Coulometric sensors, on the other hand, are based on the Faradays law of electrolysis. The sensor consists of a tube in which there is a platinum winding, to which a constant DC voltage is applied. The winding has a thin film coating, that is highly reactive with the permeating gas. As the permeant gas flows through the tube the molecules react with the coating moving through it to the platinum wires. As a result, an electrolysis reaction takes place which creates a current in the platinum wire. The current is analyzed in order to calculate the concentration of the permeant (Evans 2012, p. 1-2). All the test equipment in this study have coulometric sensors.

7.2 Rate of grease penetration

Another important barrier property of films in packaging is grease resistance for which there are several different standardized test methods. In this study only a rapid test method is used since a very small amount of oil is required to penetrate the sample for detection. A typical rapid test setup is presented in Figure 13.

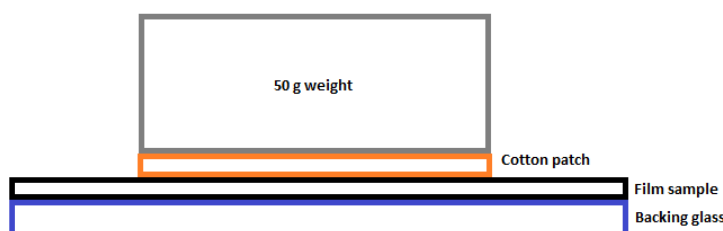


Figure 13. Grease resistance test setup.

The test is carried out at elevated temperatures under a 50 gram load in a forced-circulation oven. The film specimen is placed on a clean ground-glass backing plate so that it covers the glass. Polymeric materials may suffer from edge creep which must be taken into account in sample size. Cotton flannel rifle cleaning patches are cut into disks which have the same diameter as the 50 gram weights used in the test. The patches are placed on top and at the center of each specimen after which the weights are placed on top of the

patches. The whole test assembly is then preheated for 30 minutes in the test temperature which can be either 40°C or 60°C (ASTM F119-82 2002, p. 1-2).

When the preheat is complete the weights are removed and the grease is applied onto the cotton patches. Six drops of oil is the standard amount for testing. The test assembly is kept inside the oven during application so that the temperature remains constant. Standardized test reagents are animal oil, mineral oil and vegetable oil. However, it is also possible to use reagents like butter and tallow, but these require interlaboratory comparisons. The weights are then replaced back onto the patches. At periodic intervals the weight, cotton patch, and sample are lifted, and the glass is checked for wetting caused by the grease. The time at which the first trace of wetting can be observed is considered the time of failure. The samples which have no visible wetting are placed back into the oven (ASTM F119-82 2002, p. 2).

8. MIGRATION TESTING

In Chapter 6 it is mentioned that the components with migratory risks are primary aromatic amines (PAA), acrylate monomers and photoinitiators. The specific migration of these individual components can be analyzed using migration cells and chromatography. Photoinitiators and PAAs can be detected with liquid chromatography-mass spectrometry (LC-MS) and acrylates require the use of gas chromatography-mass spectrometry (GC-MS).

8.1 Sample preparation according to DIN EN 13130-1

Printed film samples must undergo an incubation period in a migration cell during which the migration of printing ink components occurs. Migration cells are sealed systems in which a wanted simulant is in contact with the sample in elevated temperatures. Simulants are substances which are used to mimic the influence of chemical or food contact. The combined effect of the simulant and high temperature results in an accelerated diffusion. The test time can vary from hours to days (DIN EN 13130-1, p. 29). Multiple different simulants are available for migration tests, but the most typical ones are ethanol, food oil, acetic acid and iso-octane. The concentration of the simulant can be modified in order to have an impact on the diffusion rate (Bhunia et al. 2013, p. 525). A simple migration cell is presented in Figure 14.



Figure 14. A metallic migration cell. (Norner 2018)

The incubation of film samples requires a thermostatically controlled oven or refrigerator. Migration cells are dismantled and placed inside the oven which is set at the test temperature. The standard requires three migration cells for three parallel samples. Simulant

must also be heated to the test temperature in the oven. When the test equipment and the simulant are at the same temperature the film samples can be placed inside the cells. The samples are placed so that the non-printed side is in contact with the simulant (DIN EN 13130-1, p. 44).

With the samples in place the cells are closed and the simulant is injected to the cells through a filler hole until the simulant is in contact with the sample. The cells are placed back into the oven and their temperature is monitored using a thermocouple. Temperature of the test equipment and simulant is prone to drop during the filling of the cell, which means a reheat back to the test temperature is required. The filling and sample placing must be done as fast as possible. Exposure time begins when the migration cell has reached the test temperature. However, for exposure times longer than 24 hours it is acceptable to only monitor the temperature of the oven instead of the individual samples (DIN EN 13130-1, p. 44).

After the test period the migration cells are removed from the oven and cooled. Olive oil and sunflower oil simulants require cooling to 10°C, while other simulants are cooled to 25°C. Cooling should be as rapid as possible to lower the migration rate significantly. It is important to notice that precipitation may occur with substances which have low solubility in the simulant, leading to a false result. The simulant is removed from the cell through the filler hole and is further analyzed with chromatographic methods (DIN EN 13130-1, p.44).

8.2 Chromatographic analysis

Chromatographic analysis is a separation technique, which divides the molecules in a sample according to size, shape, chemical properties or electric charge. Generally it is used to detect the components of a mixture. The sample is dissolved into a mobile phase, which, depending on the chromatographic method, can be either gas or liquid. The mobile phase is moved through a stable stationary phase. The affinity of the molecules to the two phases causes them to form columns. Higher affinity to the stationary phase causes the molecules to move towards it, while the molecules with lower affinity move away from it (Cheriyedath 2017, p. 1).

Liquid chromatography-mass spectrometry is an analyzation method which combines chromatographic separation and mass spectrum detection. It can be used to determine the elemental composition and structural elucidation of a liquid sample. Liquid chromatographic techniques consist of High Performance Liquid Chromatography, Capillary Electrophoresis and Capillary Electrochromatography (Pitt 2009, p. 19).

LC-MS test equipment consists of a liquid chromatography assembly, an ion generation unit, a mass analyzer, and a mass spectrometric data acquisition. The sample is separated using liquid mobile phase after which the sample species are sprayed into an atmospheric

ion source. The species convert into ions which transfer to the mass analyzer. The ions are separated according to their mass to charge ratio. A detector counts the number of ions and also the signal they generate is amplified. A mass spectrum can then be created with the ion signal as a function of the mass to charge ratio (Parasuraman et al. 2014, p. 49). A setup of a liquid chromatographic test system is displayed in Figure 15.

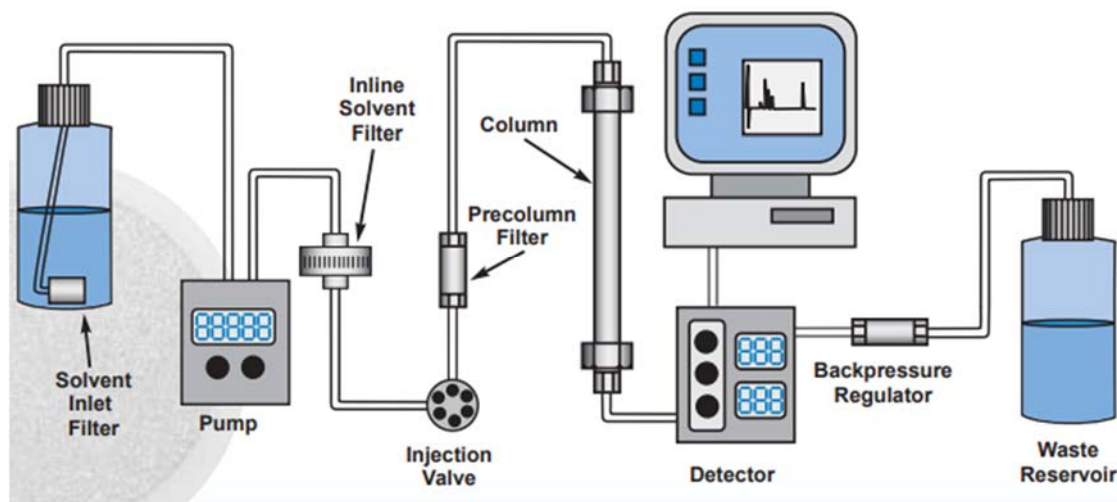


Figure 15. Liquid chromatography setup. (Wegner et al. 2004)

Gas chromatographic systems are able to analyze liquid solutions and collections of molecules absorbed onto a surface. Differently to liquid chromatography, the mobile phase is gaseous. The sample is volatilized by exposing it to a zone, which is kept at temperatures of 200°C to 300°C. A carrier gas transfers the sample to a separation section consisting of fused-silica tubular capillary with a thin polymer film coating. Typical carrier gases are argon, helium, nitrogen and hydrogen (Stashenko et al. 2014, p. 1). Gas chromatography-mass spectrometry apparatus is presented in Figure 16.

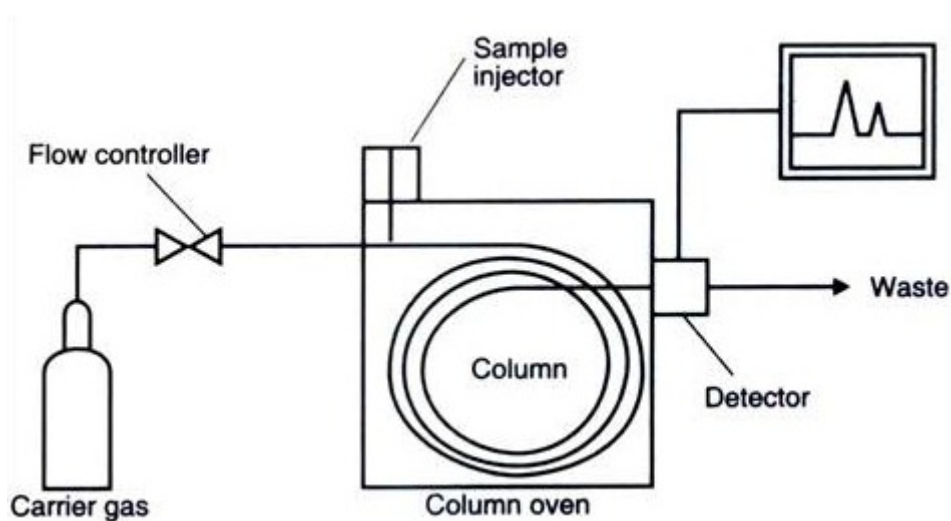


Figure 16. Schematic presentation of gas chromatography-mass spectrometry. (Kumar 2018)

Molecules of the sample are partitioned according to their chemical structure between the carrier gas stream and the polymer coating, as they move through the separation section. At the end of the separation section is a detection system, which measures the electric signal generated by the sample molecules. Depending on the detector the electric signal can be created due to physical properties of the molecules, such as thermal conductivity, or a physiochemical process like electron capture (Stashenko et al. 2014, p. 1-2).

The use of headspace sampling makes it possible to analyze individual substances faster and more accurately. A vial containing the liquid sample is heated during which the heavier sample matrix remains liquid, while the more volatile substances form a gas phase called the headspace. The volatile substances may then be extracted from the vial and injected into the GC-MS. A lot of time is saved by eluting only a part of the sample. Headspace method also reduces the possibility for overlapping peaks in the chromatogram (Stashenko et al. 2014, p. 9).

9. TEST METHODS AND SAMPLES

Sample preparation for migration testing must be done carefully to produce almost identical parallel samples without contaminants. All parts of the test cycle require precise monitoring of external variables. Test methods and sample printing are covered in this section. Also included is a total list of the sample pool.

9.1 Sample printing

The samples for migration tests were prepared using a Flexiproof 100/UV printing system, which is presented in Figure 17. It is a laboratory scale version of a flexographic printing press, but works similarly to a full sized printing press.



Figure 17. Flexiproof 100/UV printing press. (RK PrintCoat Instruments Ltd. 2018)

Film samples of PE, PP, PET, and PA-6,6 were cut to 105 mm x 297 mm size. Thickness of the samples was measured with Octagon The Film Thickness Measurement Unit GPA-Cap, so that the samples would be as identical as possible. Thickness measurements are conducted following standards DIN 53370 and ISO 4593. Using a capacitive measurement technique, the Octagon scans the whole sample measuring the thickness from 200 different points. The results were used to produce a comprehensive thickness profile of each sample. Sample thickness was allowed to vary $\pm 5\%$ of the thickness reported by the film manufacturers.

The anilox roll used in sample printing was ceramic, and had a total cell volume of 5 cm³/m², and 400 lines per inch, which is approximately 158 lines per centimeter. This would theoretically result in a total coatweight of 1,5 g/m² of ink transferred onto a non-absorbent substrate. Total area printed onto each sample was 75 mm x 240 mm. Blue UV curing ink was used for the printing. The samples were not cured using the inline UV unit of the Flexiproof, instead an offline curing system was used. The Fusion UV F300S/LT-6 system has a 120 W/cm mercury lamp and a conveyor belt. The speed of the conveyor belt was set at 40 m/min. The output of the lamp was constantly monitored during printing. The different UV wavelengths and output can be found in Table 1.

Table 1. UV light wavelengths and output.

WAVELENGTH	PEAK INTENSITY	OVERALL DOSAGE
UVA (315-400 nm)	58,6 +/-0,5 mJ/cm ²	941 +/- 10 mW/cm ²
UVB (280-315 nm)	48,9 +/- 0,5 mJ/cm ²	837 +/- 10 mW/cm ²
UVC (100-280 nm)	11,4 +/- 0,5 mJ/cm ²	193 +/- 10 mW/cm ²
UVV (395-455 nm)	75,4 +/- 1,0 mJ/cm ²	1246 +/-10 mW/cm ²

After curing, the thickness of the sample was measured again to see the total amount of ink transferred onto the substrate. The thickness of the ink film could be determined from the subtraction of the printed and non-printed sample. From the thickness of the ink film, it was possible to calculate the total volume of ink on the sample, because according to the manufacturer, density of the cured ink was 1 g/cm³. The coatweight target of ink was 1,5 g/m² +/- 0,1 g/m². Printed samples are presented in Figure 18.

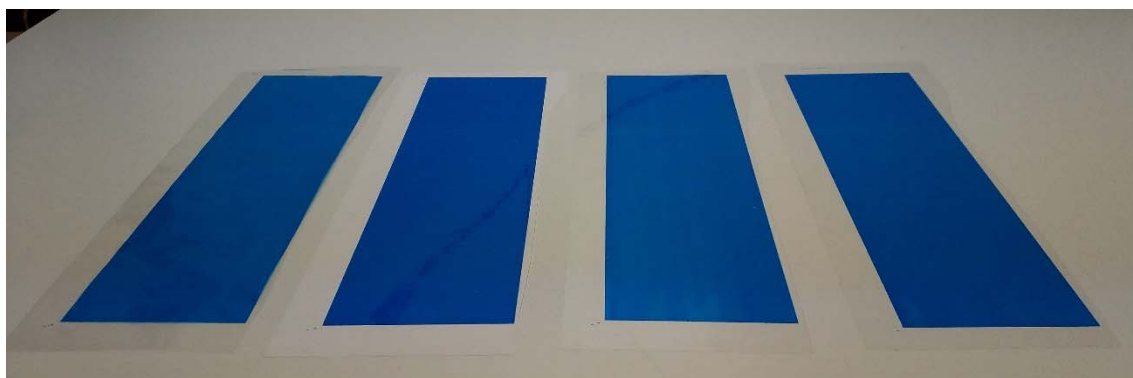


Figure 18. A photograph of the printed film samples.

The fully complete samples were wrapped in aluminum foil in order to prevent contamination before migration tests. The films were also protected from external stress and strain.

9.2 Film barrier tests

Material permeability tests were conducted at the Tampere University of Technology in the Laboratory of Paper Converting and Packaging Technology. The tests conducted are listed in Table 2.

Table 2. Permeability tests and standards.

TEST	STANDARD	EQUIPMENT
Water vapor transmission rate	DIN 53122:2	MOCON AquaTran 1G
Oxygen transmission rate	ASTM D3985 and F1927	MOCON Ox-Tran 2/21 MH
Carbon dioxide transmission rate	ASTM F2476-05	MOCON PermaTran C 4/41
Grease resistance test	ASTM F 119-82	-

The tests included thickness measurements. Water vapor and oxygen transmission rates were tested at 23°C with 50% relative humidity while the transmission rate of carbon dioxide was measured at 23°C with 0% relative humidity. The grease resistance test was conducted with olive oil at 40°C.

9.3 Migration tests

As mentioned before, the migration of primary aromatic amines, acrylate monomers and photoinitiators was studied using chromatography. The printed samples were prepared for chromatographic tests according to DIN EN 13130-1. Simulants were selected following standards EN 1186-14 and DIN EN 13130-1. Simulants and standards are listed in Table 3.

Table 3. List of simulants used.

MIGRANT	SIMULANT	STANDARD
Photoinitiator	Iso-octane 98,5%	EN 1186-14
Acrylate monomer	Ethanol 95%	EN 1186-14
Primary aromatic amine	Acetic acid 3%	DIN EN 13130-1

In food contact testing, iso-octane and ethanol 95% are typically used together to simulate fatty foodstuffs for materials which cannot be tested in olive oil. The test times are significantly shorter when compared to test times in vegetable oil. However, since the aim of this thesis was to study the migration of substances from printing ink under worst possible conditions, the use of aggressive simulants was necessary. Iso-octane would have also been an interesting simulant for acrylate monomers, but it is not a viable option, since acrylates are studied using headspace GC-MS. Iso-octane is a volatile substance which would mix in the headspace with the acrylates resulting in overlapping of peaks in the chromatogram. Instead, 95% ethanol was used. Acetic acid was chosen for the primary aromatic amines due to their hydrophilic character. The simulant is also polar, which means the substances have high affinity towards each other.

The incubation time in a migration cell was 10 days and the temperature of the cell was set to 40°C. The test time was set according to EU Regulation 10/2011, which states that the test conditions mimic long term storage at room temperature or below and also short term heating. All the parts of migration tests were conducted at Wessling GmbH.

9.4 SAMPLE POOL

According to DIN 13130-1 specific migration tests require three parallel samples, but due to the high number of samples only two parallels samples were tested. The sample pools for specific migration of ink components are listed in the Table 4, 5, and 6. The sample pools consist of 95 µm clear PE, 95 µm and 140 µm white PE, 58 µm clear PP, 58 µm and 90 µm white PP, 38 µm clear PA-6,6 and also 12 µm, 23 µm and 30 µm PET films. The samples were marked with sample number starting from S1. The materials are named according to their abbreviation and thickness. The letter in the end describes if the film is white W or clear C. PET and PA films were only clear.

Table 4. Sample pool for specific migration test of PAAs.

MATERIAL	SAMPLE	FILM THICKNESS (µm)	INK COATWEIGHT (g/m ²)
PA-6,6	S1	38,1	1,4
PA-6,6	S3	38,3	1,4
PE95C	S27	96,1	1,4
PE95C	S28	94,3	1,4
PE95W	S29	94,9	1,4
PE95W	S30	94,0	1,4
PE140W	S58	138,7	1,4
PE140W	S62	138,6	1,5
PP58C	S15	54,0	1,4
PP58C	S16	56,1	1,4
PP58W	S41	57,6	1,4
PP58W	S46	57,2	1,4
PP90W	S29	91,0	1,4

PP90W	S30	90,9	1,4
PET12	S18	12,0	1,4
PET12	S21	12,1	1,4
PET23	S47	22,9	1,4
PET23	S52	23,0	1,4
PET30	S54	29,6	1,4
PET30	S56	29,1	1,4

The sample pool for the specific migration test of primary aromatic amines is presented in Table 4. The samples for each specific migration test were selected so that the thickness of the sample and the ink coatweight were as similar among each parallel sample as possible. The ink coatweight of the PAA migration samples were mostly 1,4 g/m².

Table 5. Sample pool for specific migration test of acrylate monomers.

MATERIAL	SAMPLE	FILM THICKNESS (µm)	INK COATWEIGHT (g/m ²)
PA-6,6	S4	38,1	1,6
PA-6,6	S5	37,9	1,6
PE95C	S25	97,0	1,6
PE95C	S26	93,9	1,6
PE95W	S31	96,2	1,6
PE95W	S32	94,5	1,6
PE140W	S58	138,7	1,4
PE140W	S62	138,6	1,5
PP58C	S9	55,2	1,6
PP58C	S12	54,4	1,6
PP58W	S43	56,4	1,6
PP58W	S44	56,9	1,6
PP90W	S39	90,9	1,6
PP90W	S40	90,1	1,6
PET12	S17	11,9	1,5
PET12	S19	12,2	1,6
PET23	S49	22,6	1,6
PET23	S51	22,7	1,5
PET30	S53	29,6	1,5
PET30	S55	29,1	1,5

The sample pool for specific migration test of acrylate monomers is listed in Table 5. The ink coatweight was mostly at 1,6 g/m².

Table 6. Sample pool for specific migration test of photoinitiators.

MATERIAL	SAMPLE	FILM THICKNESS (µm)	INK COATWEIGHT (g/m ²)
PA-6,6	S2	37,4	1,5
PA-6,6	S7	37,6	1,5
PE95C	S23	93,8	1,4

PE95C	S24	94,2	1,4
PE95W	S33	97,2	1,4
PE95W	S34	95,4	1,5
PE140W	S59	139,6	1,5
PE140W	S61	138,7	1,5
PP58C	S11	55,1	1,5
PP58C	S14	54,9	1,5
PP58W	S42	56,6	1,4
PP58W	S45	57,6	1,4
PP90W	S35	91,2	1,5
PP90W	S36	91,2	1,6
PET12	S20	11,8	1,4
PET12	S22	11,6	1,4
PET23	S48	22,7	1,5
PET23	S50	22,7	1,5
PET30	S63	29,9	1,4
PET30	S64	29,5	1,4

The sample pool for specific migration test of photoinitiators is presented in Table 6. The ink coatweight varied between 1,4 and 1,6 g/m², which is still in acceptable tolerance.

10. RESULTS AND DISCUSSION

All the test results are presented and analyzed in this chapter. The analysis consists of a comparison of the face stock material behavior in permeability and migration tests. Also included is an evaluation of the possible correlation between the migration and permeability results.

10.1 Face stock material comparison

Water vapor, oxygen, carbon dioxide, and grease transmission rate results are compared to see the difference in permeability properties of different face stock materials. A comparison of migration results of photoinitiators, acrylate monomers, and primary aromatic amines reviews the potential of using polymeric materials as barriers for different migrants.

10.1.1 Permeability test results

Transmission rate results are presented using histograms to show the impact of material selection and film thickness on permeability properties. Higher transmission rates equal higher permeability, and thus poorer barrier properties. Comprehensive permeability test results are in Appendix A.

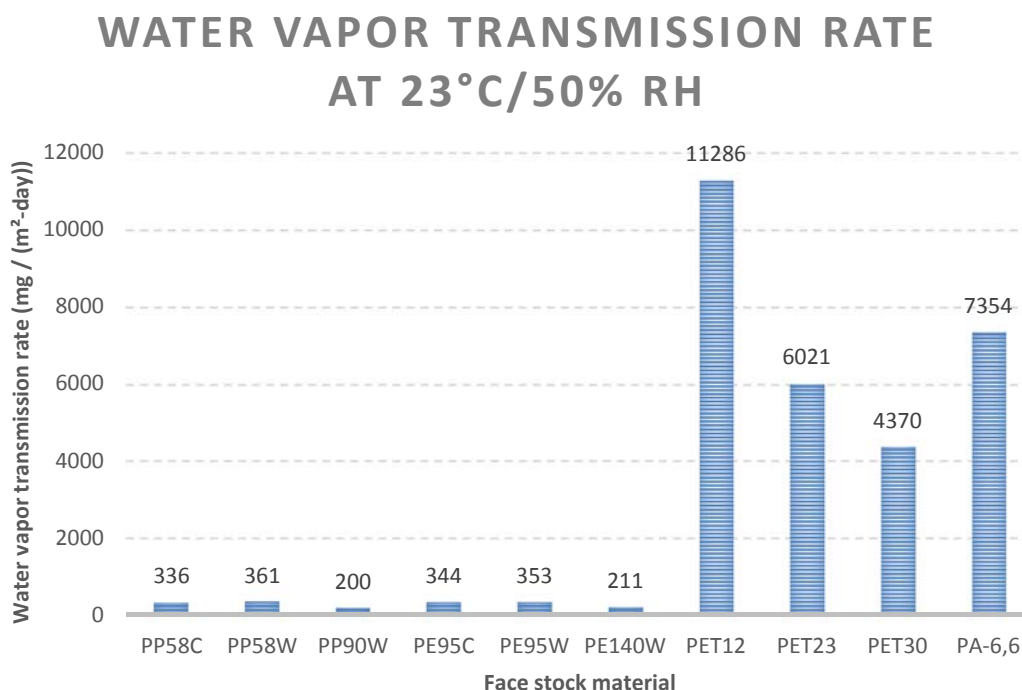


Figure 19. A histogram of the H₂O vapor transmission rate of different face stocks.

Water vapor transmission rate results are displayed in Figure 19. Water vapor transmission rate is reported as permeated mass per area in 24 hours. PP films have the best water vapor barrier with the lowest thickness. PE also provides a similar barrier but requires a much higher film thickness. PA-6,6 and PET are polar polymers due to which they have higher affinity towards water resulting in increased WVTR.

Oxygen (O_2 TR) and carbon dioxide (CO_2 TR) transmission rates are reported as permeated volume per area in 24 hours. Oxygen transmission rate of PET and PA is significantly lower than of PE and PP. Low oxygen permeability of PET and PA are a result of high crystallinity and polarity. Less crystalline PE and PP have a very high oxygen transmission rate despite their higher thickness compared to PET and PA. It would seem that white PP films have higher oxygen transmission rate than clear films. Oxygen transmission rate results are presented in Figure 20.

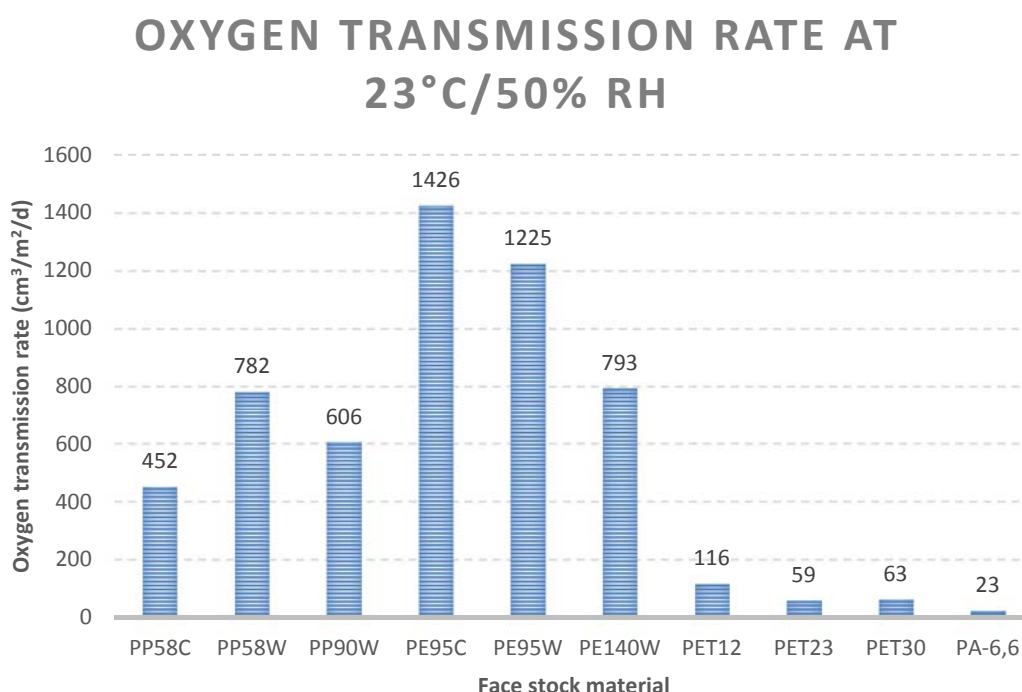


Figure 20. A histogram of the O_2 transmission rate of different face stocks.

Overall results of carbon dioxide transmission rate are similar to oxygen transmission rate. PE has the worst performance while PET and PA have the best performance. Both oxygen and carbon dioxide are non-polar gases so PE and PP have higher affinity towards them. According to the results, carbon dioxide transmission rate is higher in white films. The films are colored using titanium oxide (TiO_2), which is a polar molecule. Since PE and PP are non-polar molecules it is possible that the polymer matrix has more free volume since the polymer and colorant have low affinity towards each other. This would also explain the higher oxygen transmission rate of PP58W and PP90W. Carbon dioxide transmission rate results are presented in Figure 21.

CARBON DIOXIDE TRANSMISSION RATE AT 23°C/0% RH

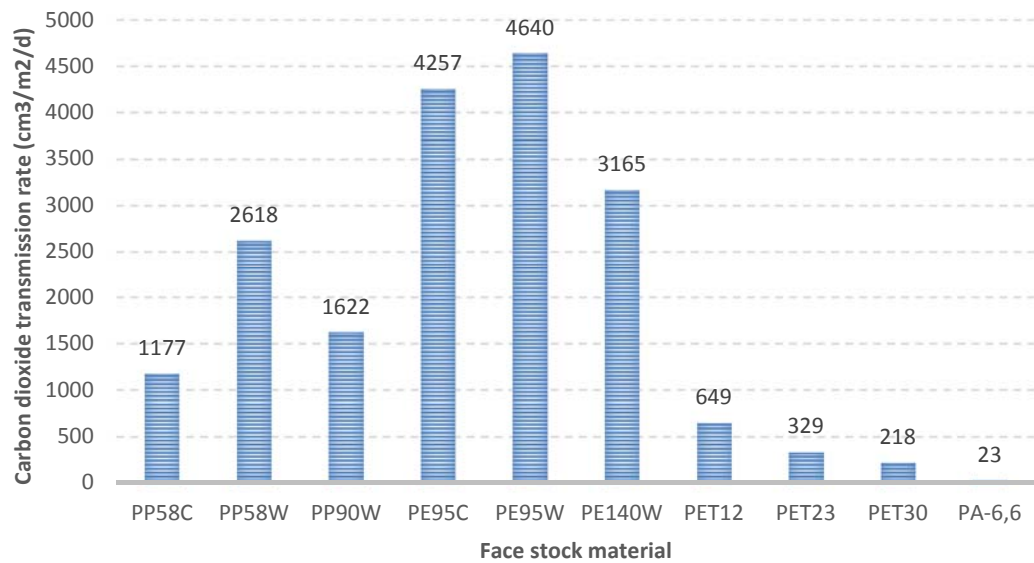


Figure 21. A histogram of the CO₂ transmission rate of different face stocks.

Rate of grease transmission test results are presented in hours it takes for the grease to penetrate the sample. A boxplot of the grease penetration results is presented in Figure 22.

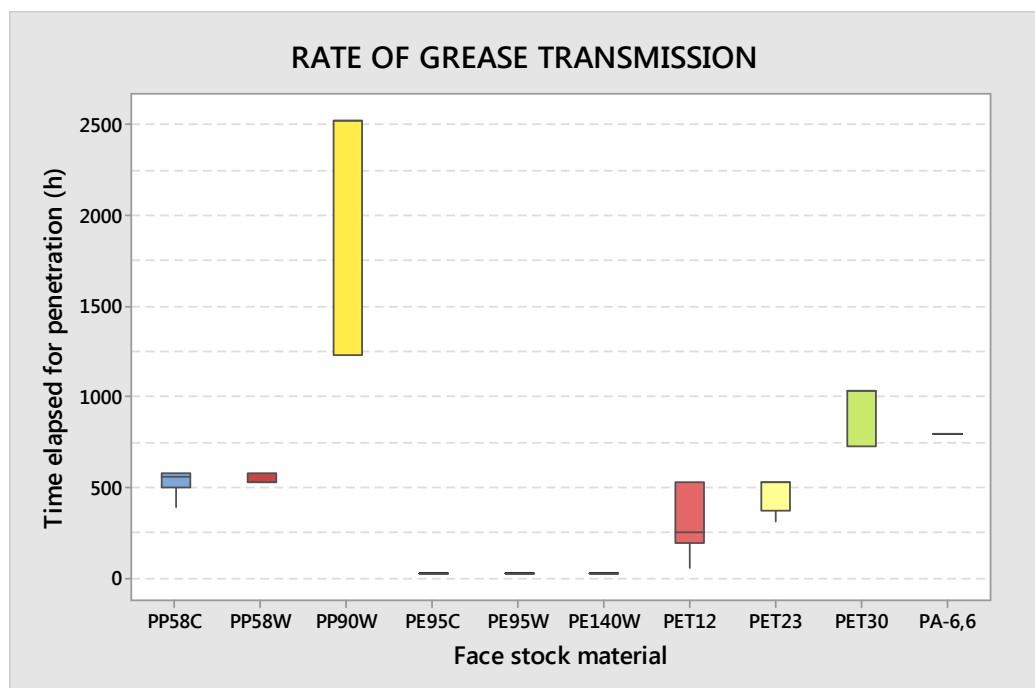


Figure 22. A boxplot of the rate of grease transmission of different face stocks.

Vegetable oils are typically non-polar or low polarity substances, which consist of triglycerides. Olive oil used for the tests is non-polar, which results in higher transmission rates for PE and PP. It took only 24 hours for olive oil to penetrate all the PE samples, while PP films with lower thickness perform significantly better taking several hundreds of hours to failure. PA and PET have the best grease resistance with the lowest thickness.

10.1.2 Migration of photoinitiators

Multiple different photoinitiators are used in the formulation of UV curing inks. The blue UV ink used for sample printing consists of at least the photoinitiators listed in Table 7. The comprehensive formulation of the ink is only known to the manufacturer so it is impossible to know the concentration of individual photoinitiators. Photoinitiator migration results are combined in the Appendix B.

Table 7. *A list of the photoinitiators scanned using the LC-MS.*

Photoinitiator	CAS number
Benzophenone	119-61-9
2-Methylbenzophenone	131-58-8
4-Methylbenzophenone	134-84-9
Methyl-2-benzoylbenzoate	606-28-0
4-Hydroxybenzophenone	1137-42-4
4-Phenylbenzophenone	2128-93-0
4-Methoxybenzophenone	611-94-4
Michlers Ketone	90-94-8
2-Carboxybenzophenone	85-52-9
Michlers Ethylketone	90-93-7
1-Chloro-4-propoxy-9H-thioxanthen-9-one (CPTX)	142770-42-1
2-Isopropylthioxanthone (ITX)	5495-84-1
Ethyl-4-dimethylaminobenzoate	10287-53-3
2-Ethylhexyl-4-(dimethylamino)benzoate	21245-02-3
Phenylbis(2,4,6-trimethylbenzoyl)phosphin oxide	162881-26-7
Diphenyl-(2,4,6-trimethylbenzoyl)-phosphin oxide	75980-60-8
N-Phenylglycine	103-01-5
2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone	106797-53-9
1-Hydroxycyclohexylphenylketone	947-19-3
2-Methyl-4'-(Methylthio)-2-morpholinopropiophenone	71868-10-5
2-Benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone	119313-12-1
4-(Dimethylamino)benzophenone	530-44-9
Leucomalachite green	129-73-7
2,4-Diethyl-9H-thioxanthen-9-one (DETX)	82799-44-8
2,2-Diethoxyacetophenone	6175-45-7
Esacure 1001 M	272460-97-6
Leucocrystal Violet	603-48-5

The results of migrated photoinitiators are displayed in Figures 23 to 30. Migration of components is reported in milligrams of migrant per one kilogram of simulant.

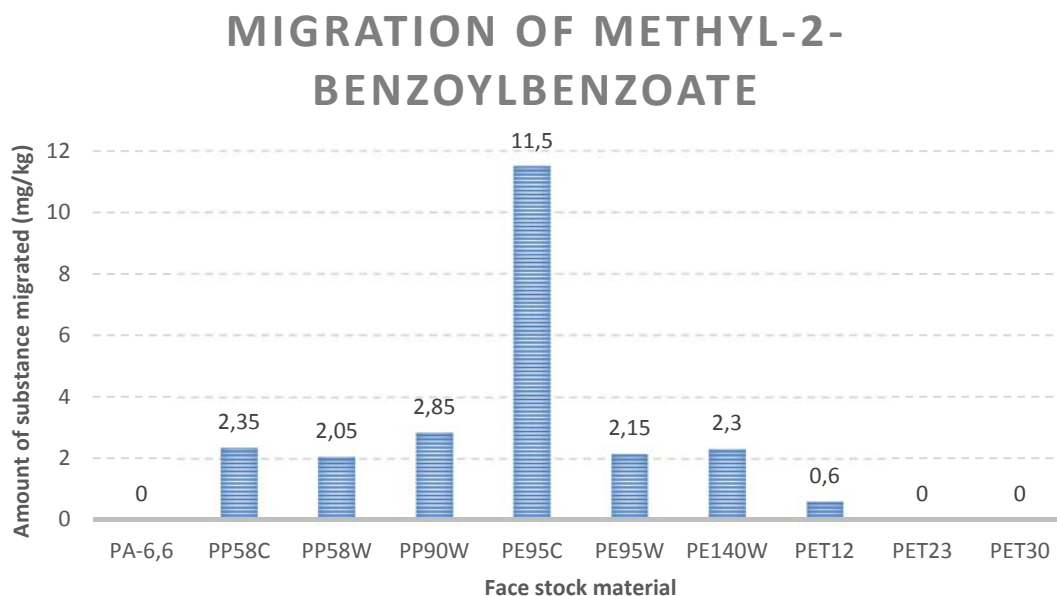


Figure 23. A histogram of the migration results of methyl-2-benzoylbenzoate.

Migration results of methyl-2-benzoylbenzoate are presented in Figure 23. Methyl-2-benzoylbenzoate is a low polarity, lipophilic ester with a molecular weight of 240,25 g/mol. (Aparacio et al. 2014, p. 190). Since iso-octane is also lipophilic, the simulant and migrant have high affinity for each other. Low polarity of the migrant seems to also result in a more aggressive migration in PE and PP. On the other hand, there is little to no migration in PET and PA most likely due to high polarity and crystallinity of the substrates.

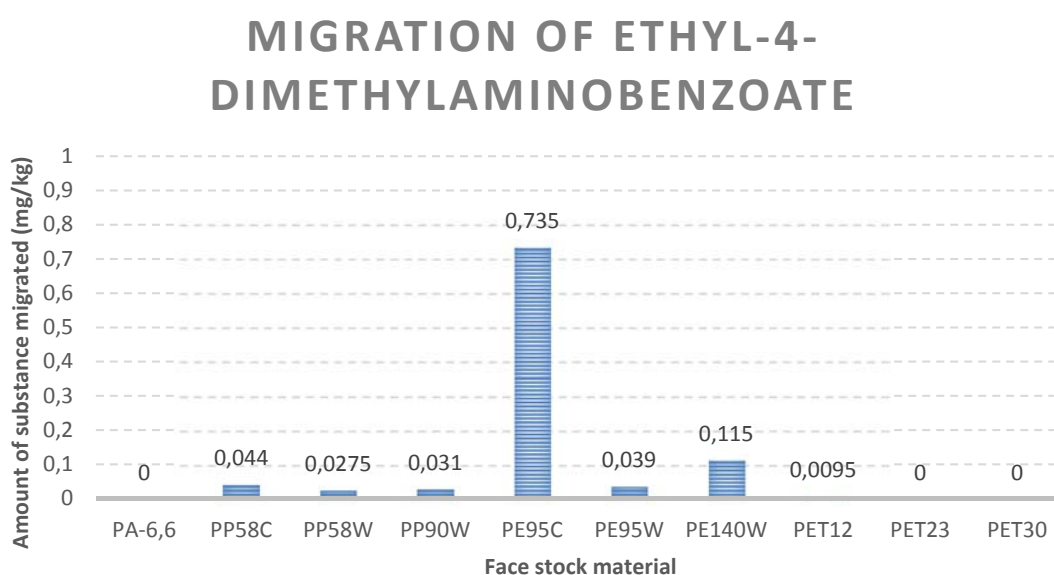


Figure 24. A histogram of the migration results of ethyl-4-dimethylaminobenzoate.

Another migrating ester is ethyl-4-dimethylaminobenzoate (EDAB). The amount migrated through each face stock is presented in Figure 24. EDAB has a slightly higher polarity and lower lipophilicity than methyl-2-benzoylbenzoate and a lower molecular weight at 193,24 g/mol (Aparacio et al. 2014, p. 190). Similar migration behavior can be observed in all the face stocks as with methyl-2-benzoylbenzoate, but in significantly smaller quantities. Since migration of components is dependent on concentration gradient, it seems that the amount of the migrant in the ink formulation is initially lower. The migration of 2-ethylhexyl-4-(dimethylamino)benzoate (EHDAB) follows a similar pattern. The migration test results of EHDAB are presented in Figure 25.

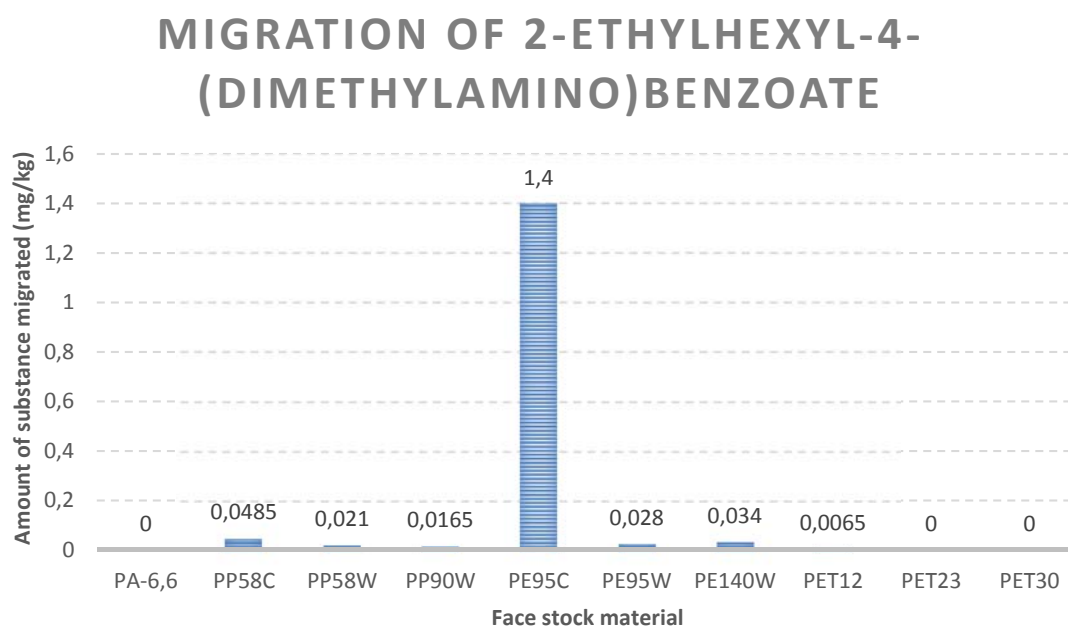


Figure 25. A histogram of the migration results of 2-ethylhexyl-4-(dimethylamino)benzoate.

EHDAB has a the functional group of an ester and is highly lipophilic. It is a non-polar substance with the molecular weight of 277,40 g/mol (Aparacio et al. 2014, p. 190). Theoretically, it would be likely that the chemical nature of EHDAB resulted in significant migration through the non-polar substrates. However, the total amount migrated is very low except with PE95C, which indicates that the amount of EHDAB in the ink formulation is low.

Benzophenones are non-polar aromatic ketones. They have high lipophilicity and low molecular weight resulting in typical migration to fatty simulants (Aparacio et al. 2014, p. 190&192). Two different benzophenone migrants were found in the migration tests: 4-phenylbenzophenone and 2-carboxybenzophenone. The migration results of 4-phenylbenzophenone are displayed in Figure 26 and the results of 2-carboxybenzophenone migrants in Figure 27.

MIGRATION OF 4-PHENYLBENZOPHENONE

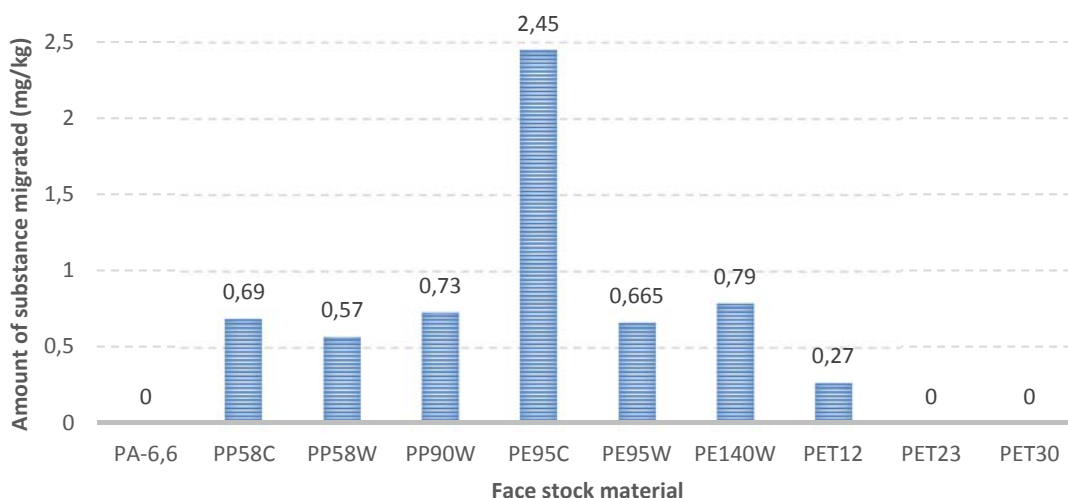


Figure 26. A histogram of the migration results of 4-phenylbenzophenone.

Significant migration can be observed in the case of 4-phenylbenzophenone, which has a molecular weight of 258, 31 g/mol (Aparacio et al. 2014, p. 190). The highest quantity migrated is through clear PE film and the lowest through PET and PA films. It is an expected result considering the chemical properties of benzophenones. However, the results suggest, that there is no thickness dependence on the migration results. The crystallinity degree of the material seems to be an influencing factor since the amount migrated is lower with higher crystallinity materials.

MIGRATION OF 2-CARBOXYBENZOPHENONE

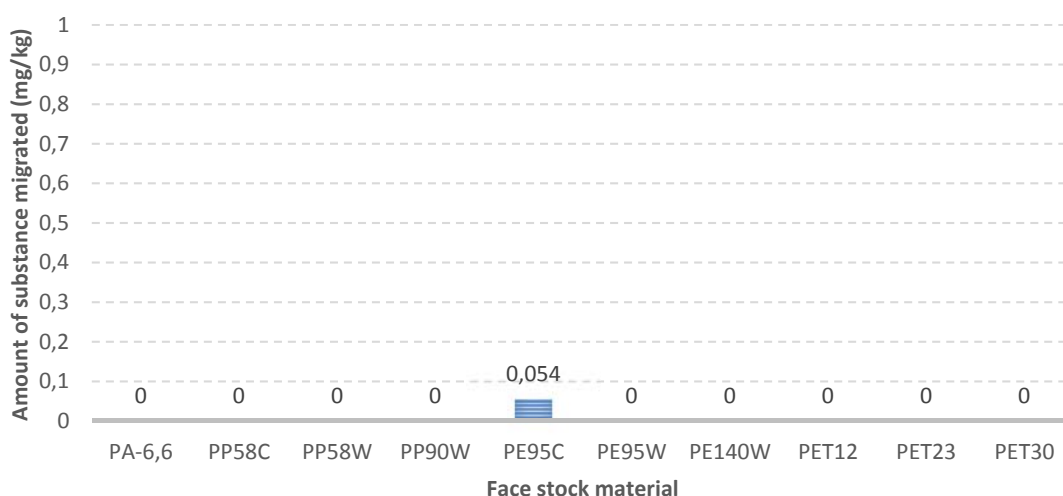


Figure 27. A histogram of the migration results of 2-carboxybenzophenone.

The migration of 2-carboxybenzophenone occurs only through PE95C. Similarly to 4-phenylbenzophenone it is a high lipophilic substance with molecular weight of 226,23 g/mol (Aparacio et al. 2014, p. 190). Since the migrant has high affinity for the simulant and non-polar films, the results suggest that its concentration in the ink is very low.

Three more aromatic ketone migrants were found in the specific migration tests: 1-hydroxycyclohexylphenylketone, 2-methyl-4'-(methylthio)-2-morpholinopropiophenone and 2,4-diethyl-9H-thioxanthene-9-one. The test results of 1-hydroxycyclohexylphenylketone are displayed in Figure 28.

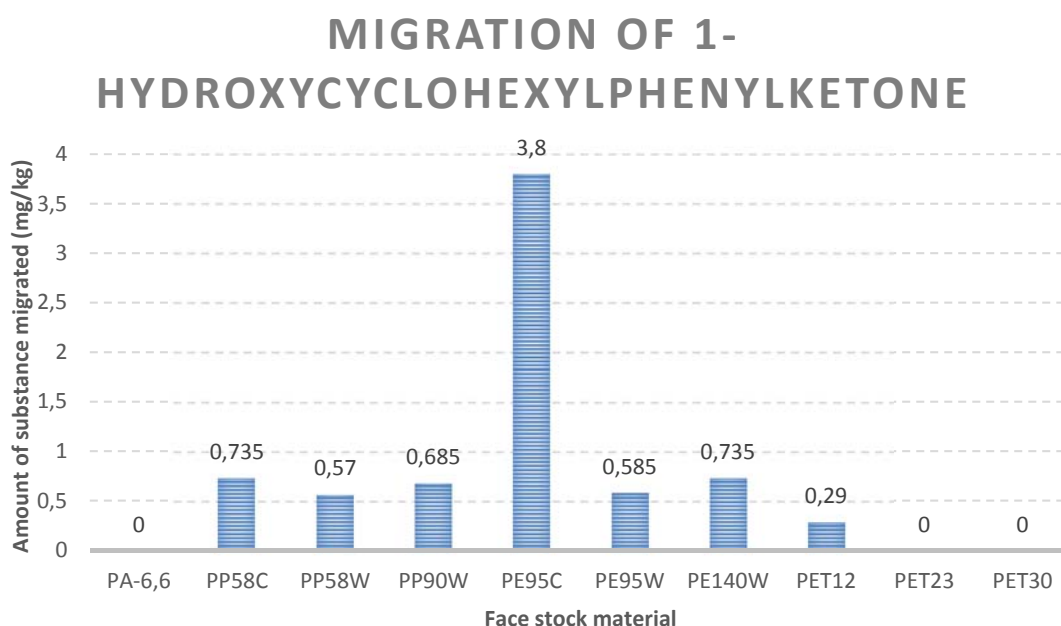


Figure 28. A histogram of the migration results of 1-hydroxycyclohexylphenylketone.

The molecular weight of 1-hydroxycyclohexylphenylketone is 204,26 g/mol (Aparacio et al. 2014, p.190) The component is a polar molecule with lower lipophilicity than any other migrated photoinitiator. Despite being chemically different to the simulant, the PI migrates through all non-polar substrates in significant quantities and also manages to penetrate through the 12 μm PET film. The migration through PET film can be explained with the polar nature of the molecule, but the behavior in PE and PP films is a result of the low molecular weight and size of the molecule.

The migration of 2-methyl-4'-methylthio-2-morpholinopropiophenone (MTMP) is significantly lower, compared to other migrated aromatic ketones. First of all, it is possible that the concentration of MTMP is very low in the ink formulation. However, the physicochemical properties of MTMP also indicate towards lower migration. It has a molecular weight of 279,40 g/mol and high polarity which means that the affinity for the simulant and PE and PP is low (Aparacio et al. 2014, p. 190). No migration through PET and PA films could be detected. The migration results of MTMP can be seen in Figure 29.

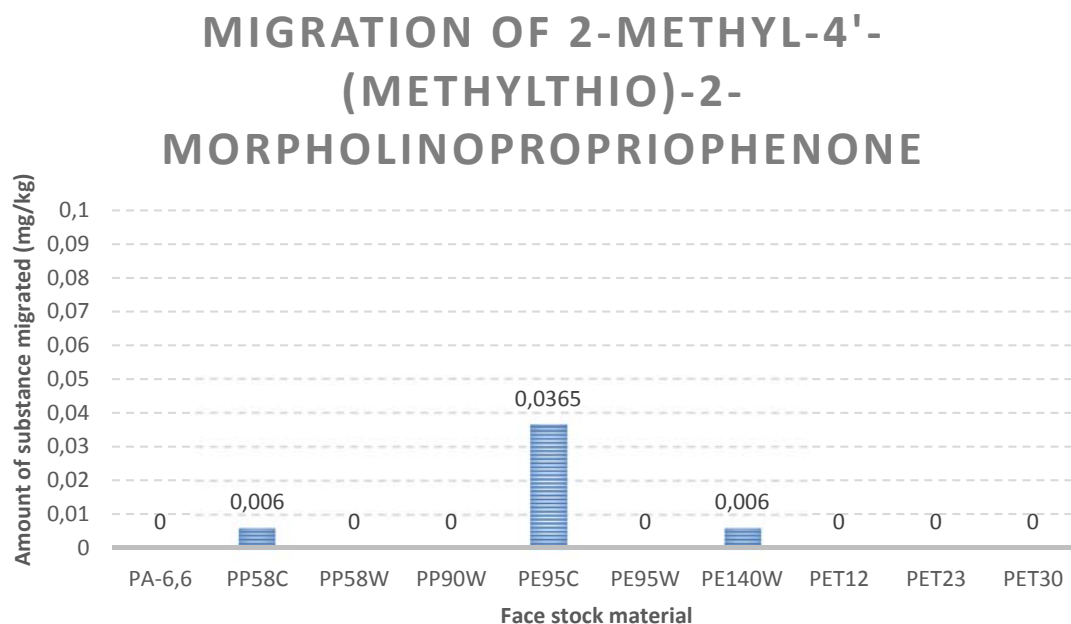


Figure 29. A histogram of the migration results of 2-methyl-4'-(methylthio)-2-morpholinopropiophenone.

The last migrant is 2,4-diethyl-9H-thioxanthen-9-one (DETX), which is a heterocyclic aromatic ketone. The photoinitiator is non-polar high lipophilic substance with a molecular weight of 268,37 g/mol (Aparacio et al. 2014, p.190). The total amounts migrated through the substrates are presented in Figure 30.

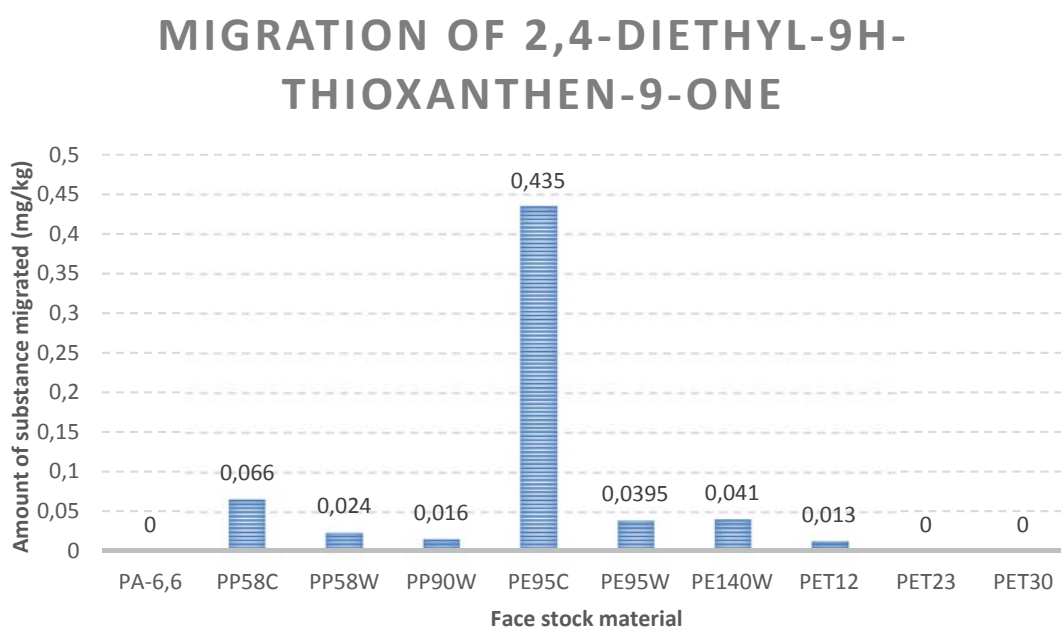


Figure 30. A histogram of the migration results of 2,4-diethyl-9H-thioxanthen-9-one.

Migration of DETX is at a very low level in all the substrates. The lipophilicity of the photoinitiator results in higher migration levels with non-polar substrates. Molecule size and shape could be the contributing factors to low migration behavior, since the photoinitiator is heterocyclic. It is also very likely that the amount of this PI used in the ink is very low.

Combined results of photoinitiator migration indicate, that with non-polar substrates with high thickness the migration is not visibly dependent on the thickness level. Instead, the crystallinity degree of materials seems to have more impact. Also, the presence of TiO₂ in the polymer matrix seems result in lower migration levels in polyethylene films. Thickness dependence can, however, be seen with PET films of lower thickness, since the only film suffering of migration is the 12µm PET and no migration is observed in the 23µm and 30µm variants. The affinity of the photoinitiator for the simulant and the substrate seems to also have an influence on the migration behavior, but is not always a key factor.

10.1.3 Migration of acrylate monomers

Acrylate monomers react with oligomers during UV curing forming polymer chains with high molecular weight. The monomers left unreacted are prone to migration due to their low molecular weight. Possible acrylate monomer migrants are listed in Table 8. The specific migration test results of acrylate monomers are in the Appendix C.

Table 8. *A list of the photoinitiators scanned using the headspace GC-MS.*

Acrylate monomer	CAS number
2-Ethylhexyl acrylate	103-11-7
Benzyl methacrylate	2495-37-6
Butyl acrylate	141-32-2
Butyl methacrylate	97-88-1
Methyl methacrylate	80-62-6
Methyl acrylate	96-33-3
Ethyl acrylate	140-88-5
Ethylene dimethacrylate	97-90-5
Hexamethylene diacrylate	13048-33-4

All the tested acrylates are esters with a molecular mass in the same range with photoinitiators. Esters are lipophilic due to which the migration to fatty food simulant ethanol would be very likely. However, the tests showed no sign of acrylate monomer migration. A possible reason for this is that the majority of the monomers have reacted with oligomers. The quantity of the monomers left unreacted is so small that the migrants cannot be detected. The barrier function of the face stock materials may also be sufficient to block the migration of acrylates.

10.1.4 Migration of primary aromatic amines

Primary aromatic amines are used as colorants, and consist of an aromatic ring, and an amine functional group. They are typically trapped inside the ink matrix after curing, but due to their low molecular weight possess a risk for migration. A list of possible PAA migrants is presented in Table 9.

Table 9. *A list of the PAAs scanned using the LC-MS.*

Primary aromatic amine	CAS number
2,4,5-Trimethylaniline	137-17-7
p-Cresidine	120-71-8
2,4-Toluenediamine	95-80-7
2-Methyl-5-nitroaniline	99-55-8
2-Naphthylamine	91-59-8
3,3'-Dichlorobenzidine	91-94-1
3,3'-Dimethoxybenzidine	119-90-4
3,3'-Dimethyl-4,4'-diaminodiphenylmethane	838-88-0
3,3'-Dimethylbenzidine	119-93-7
4,4'-Diaminodiphenylmethane	101-77-9
4,4'-methylen-bis-(2-chloroaniline)	101-14-4
4,4'-Oxydianiline	101-80-4
4,4'-Thiodianiline	139-65-1
4-Aminoazobenzene	60-09-3
4-Aminodiphenyle	101-54-2
4-Chloroaniline	106-47-8
Aniline	62-53-3
Benzidine	92-87-5
o-Aminoazotoluene	97-56-3
4-Chloro-o-toluidine	95-69-2
o-Anisidine	90-04-0
o-Toluidine	95-53-4
2,4-Diaminoanisole	615-05-4
p-Toluidine	106-49-0

Amines are hydrophilic molecules, which means that they are polar. The simulant, acetic acid, is also polar resulting in high affinity between the simulant and migrant. The photometric sum of amines indicates that migration has occurred in the range of 0,02-0,03 µg/kg in all PE films and in clear PP films, but only in very small quantities. Primary aromatic amines were also found in the testing of PA samples, but since polyamides consist of amines it is very likely, that the amines detected are from the polymer matrix rather than migrants from the printing ink. However, it is not possible to single out the substances migrated, because migration levels are below the detection threshold.

The low quantity of the migrants is very likely due to the same reason as with acrylates. Either the concentration of the PAAs in the ink is very low or the cure level is sufficient

to keep the substances trapped in the ink matrix. However, even though the migration levels are very low, individually indeterminable components have still made it through the polymer matrix. Lower cure levels or the use of different inks could result in the detection of PAAs in higher amounts.

10.2 Correlation between permeability and migration results

In terms of physiochemical properties, the migrants and diffusants are very different. Photoinitiators, acrylates and PAAs are somewhat similar in their own group of chemicals, and some substances may share similar properties. A key factor in migration behavior is also the selection of the simulant. However, the test results suggest a connection between the specific migration of photoinitiators and gas permeability of oxygen and carbon dioxide in polymers. The combined results of permeability and migration tests are presented in Table 10.

Table 10. Gas and grease transmission rate of materials compared to the number of photoinitiators migrated per material.

	O ₂ TR	CO ₂ TR	WVTR	GreaseTR	Photoinitiators
PE95C	Very high	Very high	Low	Very high	8 migrants
PE95W	Very high	Very high	Low	Very high	6 migrants
PE140W	High	Very high	Low	Very high	7 migrants
PP58C	High	High	Low	Moderate	7 migrants
PP58W	High	High	Low	Moderate	6 migrants
PP90W	High	High	Low	Low	6 migrants
PET12	Low	Low	Very high	Low	6 migrants
PET23	Low	Low	High	Low	0 migrants
PET30	Low	Low	High	Low	0 migrants
PA	Very low	Very low	High	Low	0 migrants

As mentioned earlier most of the migrated PIs are to a degree lipophilic substances, and thus the affinity for the simulant is very high. Results indicate, that migration of non or low polar lipophilic photoinitiators favors non-polar polymers. Oxygen and carbon dioxide molecules have physiochemical similarities being non-polar and lipophilic. Due to this, they have a high tendency to diffuse through non-polar substrates, which can be seen with the high transmission rates in PE and PP films and lower in PET and PA. Based on the results presented in Table 10 and subchapters 10.1.1. and 10.1.2., it can be stated that the weaker the barrier of a material is to oxygen and carbon dioxide, the more prone it is to suffer from the migration of non or low polar lipophilic photoinitiators.

11. CONCLUSIONS AND FUTURE PROSPECTS

The specific migration tests resulted in the detection of photoinitiators and primary aromatic amines. The highest level of migration occurred in polypropylene and polyethylene films. Polyethylene terephthalate films with the thickness of 12 μm suffered from minor migration of photoinitiators, while no migration of any component occurred in the 23 μm and 30 μm equivalents. Polyamide films had no sign of printing ink component migration. The individual photoinitiators detected were: methyl-2-benzoylbenzoate, 4-phenylbenzophenone, 2-carboxybenzophenone, ethyl-4-dimethylaminobenzoate, 2-ethylhexyl-4-(dimethylamino)benzoate, 1-hydroxycyclohexylphenylketone, 2-methyl-4'-(methylthio)-2-morpholinopropiophenone, and 2,4-diethyl-9H-thioxanthen-9-one.

Results suggest, that the physical dimensions of the samples are irrelevant at higher thickness levels. The degree of crystallization is a more critical factor regarding the migration behavior. However, at lower thicknesses it was observed that the thicker PET films limited the migration of photoinitiators. Another factor is the selection of simulants, which, in this study, were selected according to the affinity of the migrants for the simulant to create a worst-case scenario. Different migration results may be observed using a different simulant. The effect of impact of simulants could be used as a topic for future work.

A possible correlation between the permeability properties of polymers and migration behavior of photoinitiators was found. The results indicate that polymers with high oxygen and carbon dioxide permeability are more likely to suffer from the migration of non or low polar lipophilic photoinitiators.

As a concluding remark, according to the results of this study, polyethylene terephthalate films with thickness of at least 23 μm could be used as a barrier for photoinitiators, acrylates and primary aromatic amines from printing inks.

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APPENDIX A: TRANSMISSION RATE TEST RESULTS

Table 10. WVTR results from TUT.

50 % RH / 23°C	mg / (m²-day)		
	A	B	KA
PP 58C	351.50	319.81	336
PP 58W	361.64	359.40	361
PP 90W	200.67	199.71	200
4K PE	349.74	337.86	344
PE 95W	357.90	347.31	353
PE 140W	210.74	211.22	211
PET 50	2500.70	2473.40	2487
PET 23	5971.96	6070.32	6021
PET 12	11290.18	11282.68	11286
05 PET	4430.10	4310.10	4370
PA	7197.24	7511.11	7354

Table 11. Oxygen transmission rate results from TUT.

23 °C / 50 % RH	O₂TR (cm³/m²/d)		
	A	B	KA
PP 58C	451.09	451.97	452
PP 58W	809.67	753.50	782
PP 90W	604.94	606.14	606
4K PE	1375.98	1476.26	1426
PE 95W	1262.37	1187.23	1225
PE 140W	784.21	802.72	793
PET 50	38.56	39.05	39
PET 23	58.31	58.85	59
PET 12	113.15	119.83	116
05 PET	60.97	64.31	63
PA	20.04	25.68	23

Table 12. Carbon dioxide transmission rate results from TUT.

23 °C / 0 % RH	CO ₂ TR (cm ³ /m ² /d)		
	A	B	KA
PP 58C	1184.68	1168.76	1177
PP 58W	2612.26	2624.22	2618
PP 90W	1599.23	1645.71	1622
4K PE	4338.28	4175.27	4257
PE 95W	4708.62	4571.18	4640
PE 140W	3231.32	3099.02	3165
PET 50	139.60	142.22	141
PET 23	326.83	331.30	329
PET 12	615.64	682.80	649
05 PET	224.38	211.84	218
PA	70.62	70.13	70

Table 13. Grease transmission rate results from TUT.

[illegible]

Table 14. Grease transmission rate results of PET12 & PET23 from TUT.

[illegible]

Table 15. Grease transmission rate results of PA from TUT.

[illegible]

APPENDIX B: SPECIFIC MIGRATION RESULTS FROM WESSLING

The original specific migration test reports from Wessling GmbH are included in this appendix. The reports are:

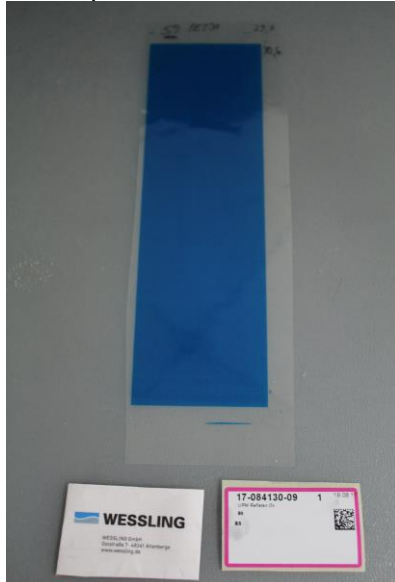
- Report No. CAL17-080476-1/hve, specific migration test of photoinitiators through PE95C and PET30 in two temperature. The report shows different numbering than reported in Chapter 9. S27 = 17-084130-15, S28 = 17-084130-16, S63 = 17-084130-13 and S64 = 17-084130-14 . The test at 20°C was used to examine the effect of temperature to the test results, but since the results were similar in the lower temperature it would suggest that the equilibrium state had been reached even in lower temperatures.
- Report No. CAL17-080476-1/hve, specific migration test of photoinitiators through PE95W, PE140W, PP58C, PP58W, PP90W, PET12, PET23 and PA-6,6.
- Report No. CAL17-145953-1/hve, specific migration test of acrylate monomers.
- Report No. CAL17-129906-1/hve specific migration test of primary aromatic amines.

Report No. CAL17-080476-1/hve

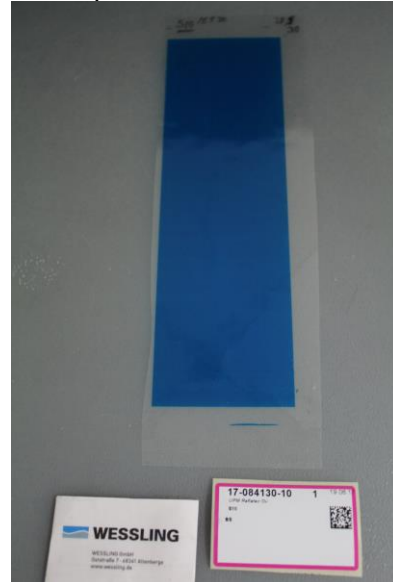
Altenberge, 25th July 2017**Material check**

- Sample receipt: 26th May 2017
- Client: UPM Raflatac Oy, Tesomankatu 31,
33101 Tampere, Finland
- Order date: in written form dated 26th May 2017
- Sampled by: Client
- Beginning of examinations: 29th June 2017
- End of examinations: 24th July 2017
- Sample No. 17-084130-09: S9
Sample No. 17-084130-10: S10
Sample No. 17-084130-11: S11
Sample No. 17-084130-12: S12
Sample No. 17-084130-13: S13
Sample No. 17-084130-14: S14
Sample No. 17-084130-15: S15
Sample No. 17-084130-16: S16
- Further information: -/-

Sample No. 17-084130-09



Sample No. 17-084130-10



Sample No. 17-084130-11



Sample No. 17-084130-12



Sample No. 17-084130-13



Sample No. 17-084130-14



Sample No. 17-084130-15



Sample No. 17-084130-16



Analysed samples/parts:

Sample No.	Sample identifier
17-084130-09	Sample complete (food contact side)
17-084130-10	Sample complete (food contact side)
17-084130-11	Sample complete (food contact side)
17-084130-12	Sample complete (food contact side)
17-084130-13	Sample complete (food contact side)
17-084130-14	Sample complete (food contact side)
17-084130-15	Sample complete (food contact side)
17-084130-16	Sample complete (food contact side)

Examination methods:

Parameter	Method	Performing place
Photoinitiators in migrate	WEX 256 (LC-MS/MS)	*
Migration preparation (single determination)	EN 13130-1 mod.	Produktanalytik Altenberge

* tested by a cooperation laboratory

Results:

1. Photoinitiators

mg/kg means mg per L isooctane

Test conditions: Isooctane, 10 d, 20 °C

Parameter	Unit	17-084130-09	17-084130-10
Benzophenone (CAS No 119-61-9)	mg/kg	< 0.01	< 0.01
2-Methylbenzophenone (CAS No 131-58-8)	mg/kg	< 0.01	< 0.01
4-Methylbenzophenone (CAS No 134-84-9)	mg/kg	< 0.01	< 0.01
Methyl-2-benzoylbenzoate (CAS No 606-28-0)	mg/kg	< 0.01	< 0.01
4-Hydroxybenzophenone (CAS No 1137-42-4)	mg/kg	< 0.01	< 0.01
4-Phenylbenzophenone (CAS No 2128-93-0)	mg/kg	< 0.01	< 0.01
4-Methoxybenzophenone (CAS No 611-94-9)	mg/kg	< 0.01	< 0.01
Michlers Ketone (DEAB) (CAS No 90-94-8)	mg/kg	< 0.01	< 0.01
2-Carboxybenzophenone (CAS No 85-52-9)	mg/kg	< 0.01	< 0.01
Michlers Ethylketone (DEAB) (CAS No 90-93-7)	mg/kg	< 0.01	< 0.01
1-Chloro-4-propoxy-9H-thioxanthen-9-one (CPTX) (CAS No 142770-42-1)	mg/kg	< 0.01	< 0.01
2,4 Diethyl-9H-thioxanthen-9-one (DETX) (CAS No 82799-44-8)	mg/kg	< 0.01	< 0.01
2-Isopropylthioxanthone (2-ITX) (CAS No 5495-84-1)	mg/kg	< 0.01	< 0.01
Ethyl-4-dimethylaminobenzoate (CAS No 10287-53-3)	mg/kg	< 0.01	< 0.01
2-Ethylhexyl-4-(dimethylamino)benzoate (CAS No 21245-02-3)	mg/kg	< 0.01	< 0.01
Phenylbis(2,4,6-trimethylbenzoyl)phosphin oxide (CAS No 162881-26-7)	mg/kg	< 0.01	< 0.01

Parameter	Unit	17-084130-09	17-084130-10
Diphenyl-(2,4,6-trimethylbenzoyl)-phosphin oxide (CAS No 75980-60-8)	mg/kg	< 0.01	< 0.01
N-Phenylglycine (CAS No 103-01-5)	mg/kg	< 0.01	< 0.01
2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (CAS No 106797-53-9)	mg/kg	< 0.01	< 0.01
1-Hydroxycyclohexylphenylketone (CAS No 947-19-3)	mg/kg	< 0.01	< 0.01
2-Methyl-4'-(methylthio)-2-morpholinopropiophenone (CAS No 71868-10-5)	mg/kg	< 0.01	< 0.01
2-Benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone (CAS No 119313-12-1)	mg/kg	< 0.01	< 0.01
4-(Dimethylamino)benzophenone (CAS No 530-44-9)	mg/kg	< 0.01	< 0.01
Leucomalachite green (CAS No 129-73-7)	mg/kg	< 0.01	< 0.01
Leucocrystal Violet (CAS No 603-48-5)		< 0.01	< 0.01
2,2-Diethoxyacetophenone (CAS No 6175-45-7)	mg/kg	< 0.01	< 0.01
4-Isopropylthioxanthone (4-ITX) (CAS No 83846-86-0)	mg/kg	< 0.01	< 0.01
Esacure one	mg/kg	< 0.01	< 0.01
2-Hydroxy-2-methylpropiophenon (CAS No 7473-98-5)	mg/kg	< 0.01	< 0.01
Esacure 1001 M (CAS No 272460-97-6)	mg/kg	< 0.01	< 0.01
Irgacure 250 (CAS No 344562-80-7)	mg/kg	< 0.01	< 0.01
Irgacure 379 (CAS No 119344-86-4)	mg/kg	< 0.01	< 0.01

Test conditions: Isooctane, 10 d, 20 °C

Parameter	Unit	17-084130-11	17-084130-12
Benzophenone (CAS No 119-61-9)	mg/kg	0.039	0.030
2-Methylbenzophenone (CAS No 131-58-8)	mg/kg	< 0.01	< 0.01
4-Methylbenzophenone (CAS No 134-84-9)	mg/kg	< 0.01	< 0.01
Methyl-2-benzoylbenzoate (CAS No 606-28-0)	mg/kg	13	11
4-Hydroxybenzophenone (CAS No 1137-42-4)	mg/kg	< 0.01	< 0.01
4-Phenylbenzophenone (CAS No 2128-93-0)	mg/kg	3.8	3.9
4-Methoxybenzophenone (CAS No 611-94-9)	mg/kg	< 0.01	< 0.01
Michlers Ketone (DEAB) (CAS No 90-94-8)	mg/kg	< 0.01	< 0.01
2-Carboxybenzophenone (CAS No 85-52-9)	mg/kg	0.14	0.10
Michlers Ethylketone (DEAB) (CAS No 90-93-7)	mg/kg	< 0.01	< 0.01
1-Chloro-4-propoxy-9H-thioxanthen-9-one (CPTX) (CAS No 142770-42-1)	mg/kg	< 0.01	< 0.01
2,4 Diethyl-9H-thioxanthen-9-one (DETX) (CAS No 82799-44-8)	mg/kg	0.44	0.46
2-Isopropylthioxanthone (2-ITX) (CAS No 5495-84-1)	mg/kg	< 0.01	< 0.01
Ethyl-4-dimethylaminobenzoate (CAS No 10287-53-3)	mg/kg	0.41	0.39
2-Ethylhexyl-4-(dimethylamino)benzoate (CAS No 21245-02-3)	mg/kg	1.7	2.0
Phenylbis(2,4,6-trimethylbenzoyl)phosphin oxide (CAS No 162881-26-7)	mg/kg	< 0.01	< 0.01
Diphenyl-(2,4,6-trimethylbenzoyl)-phosphin oxide (CAS No 75980-60-8)	mg/kg	< 0.01	< 0.01
N-Phenyglycine (CAS No 103-01-5)	mg/kg	< 0.01	< 0.01

Parameter	Unit	17-084130-11	17-084130-12
2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (CAS No 106797-53-9)	mg/kg	< 0.01	< 0.01
1-Hydroxycyclohexylphenylketone (CAS No 947-19-3)	mg/kg	4.0	3.8
2-Methyl-4'-(methylthio)-2-morpholinopropiophenone (CAS No 71868-10-5)	mg/kg	< 0.01	0.022
2-Benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone (CAS No 119313-12-1)	mg/kg	< 0.01	< 0.01
4-(Dimethylamino)benzophenone (CAS No 530-44-9)	mg/kg	< 0.01	< 0.01
Leucomalachite green (CAS No 129-73-7)	mg/kg	< 0.01	< 0.01
Leucocrystal Violet (CAS No 603-48-5)		< 0.01	< 0.01
2,2-Diethoxyacetophenone (CAS No 6175-45-7)	mg/kg	< 0.01	< 0.01
4-Isopropylthioxanthone (4-ITX) (CAS No 83846-86-0)	mg/kg	< 0.01	< 0.01
Esacure one	mg/kg	< 0.01	< 0.01
2-Hydroxy-2-methylpropiophenon (CAS No 7473-98-5)	mg/kg	< 0.01	< 0.01
Esacure 1001 M (CAS No 272460-97-6)	mg/kg	< 0.01	< 0.01
Irgacure 250 (CAS No 344562-80-7)	mg/kg	< 0.01	< 0.01
Irgacure 379 (CAS No 119344-86-4)	mg/kg	< 0.01	< 0.01

Test conditions: Isooctane, 10 d, 40 °C

Parameter	Unit	17-084130-13	17-084130-14
Benzophenone (CAS No 119-61-9)	mg/kg	< 0.01	< 0.01
2-Methylbenzophenone (CAS No 131-58-8)	mg/kg	< 0.01	< 0.01
4-Methylbenzophenone (CAS No 134-84-9)	mg/kg	< 0.01	< 0.01

UPM Raflatac Oy/CAL 17-080746-1/hve

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Parameter	Unit	17-084130-13	17-084130-14
Methyl-2-benzoylbenzoate (CAS No 606-28-0)	mg/kg	< 0.01	< 0.01
4-Hydroxybenzophenone (CAS No 1137-42-4)	mg/kg	< 0.01	< 0.01
4-Phenylbenzophenone (CAS No 2128-93-0)	mg/kg	< 0.01	< 0.01
4-Methoxybenzophenone (CAS No 611-94-9)	mg/kg	< 0.01	< 0.01
Michlers Ketone (DEAB) (CAS No 90-94-8)	mg/kg	< 0.01	< 0.01
2-Carboxybenzophenone (CAS No 85-52-9)	mg/kg	< 0.01	< 0.01
Michlers Ethylketone (DEAB) (CAS No 90-93-7)	mg/kg	< 0.01	< 0.01
1-Chloro-4-propoxy-9H-thioxanthen-9-one (CPTX) (CAS No 142770-42-1)	mg/kg	< 0.01	< 0.01
2,4 Diethyl-9H-thioxanthen-9-one (DETX) (CAS No 82799-44-8)	mg/kg	< 0.01	< 0.01
2-Isopropylthioxanthone (2-ITX) (CAS No 5495-84-1)	mg/kg	< 0.01	< 0.01
Ethyl-4-dimethylaminobenzoate (CAS No 10287-53-3)	mg/kg	< 0.01	< 0.01
2-Ethylhexyl-4-(dimethylamino)benzoate (CAS No 21245-02-3)	mg/kg	< 0.01	< 0.01
Phenylbis(2,4,6-trimethylbenzoyl)phosphin oxide (CAS No 162881-26-7)	mg/kg	< 0.01	< 0.01
Diphenyl-(2,4,6-trimethylbenzoyl)-phosphin oxide (CAS No 75980-60-8)	mg/kg	< 0.01	< 0.01
N-Phenylglycine (CAS No 103-01-5)	mg/kg	< 0.01	< 0.01
2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (CAS No 106797-53-9)	mg/kg	< 0.01	< 0.01
1-Hydroxycyclohexylphenylketone (CAS No 947-19-3)	mg/kg	< 0.01	< 0.01

Parameter	Unit	17-084130-13	17-084130-14
2-Methyl-4'-(methylthio)-2-morpholinopropiophenone (CAS No 71868-10-5)	mg/kg	< 0.01	< 0.01
2-Benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone (CAS No 119313-12-1)	mg/kg	< 0.01	< 0.01
4-(Dimethylamino)benzophenone (CAS No 530-44-9)	mg/kg	< 0.01	< 0.01
Leucomalachite green (CAS No 129-73-7)	mg/kg	< 0.01	< 0.01
Leucocrystal Violet (CAS No 603-48-5)		< 0.01	< 0.01
2,2-Diethoxyacetophenone (CAS No 6175-45-7)	mg/kg	< 0.01	< 0.01
4-Isopropylthioxanthone (4-ITX) (CAS No 83846-86-0)	mg/kg	< 0.01	< 0.01
Esacure one	mg/kg	< 0.01	< 0.01
2-Hydroxy-2-methylpropiophenon (CAS No 7473-98-5)	mg/kg	< 0.01	< 0.01
Esacure 1001 M (CAS No 272460-97-6)	mg/kg	< 0.01	< 0.01
Irgacure 250 (CAS No 344562-80-7)	mg/kg	< 0.01	< 0.01
Irgacure 379 (CAS No 119344-86-4)	mg/kg	< 0.01	< 0.01

Test conditions: Isooctane, 10 d, 40 °C

Parameter	Unit	17-084130-15	17-084130-16
Benzophenone (CAS No 119-61-9)	mg/kg	0.041	0.050
2-Methylbenzophenone (CAS No 131-58-8)	mg/kg	< 0.01	< 0.01
4-Methylbenzophenone (CAS No 134-84-9)	mg/kg	< 0.01	< 0.01
Methyl-2-benzoylbenzoate (CAS No 606-28-0)	mg/kg	8.0	15
4-Hydroxybenzophenone (CAS No 1137-42-4)	mg/kg	< 0.01	< 0.01
4-Phenylbenzophenone (CAS No 2128-93-0)	mg/kg	2.2	2.7

Parameter	Unit	17-084130-15	17-084130-16
4-Methoxybenzophenone (CAS No 611-94-9)	mg/kg	< 0.01	< 0.01
Michlers Ketone (DEAB) (CAS No 90-94-8)	mg/kg	< 0.01	< 0.01
2-Carboxybenzophenone (CAS No 85-52-9)	mg/kg	0.060	0.048
Michlers Ethylketone (DEAB) (CAS No 90-93-7)	mg/kg	< 0.01	< 0.01
1-Chloro-4-propoxy-9H-thioxanthen-9-one (CPTX) (CAS No 142770-42-1)	mg/kg	< 0.01	< 0.01
2,4 Diethyl-9H-thioxanthen-9-one (DETX) (CAS No 82799-44-8)	mg/kg	0.45	0.42
2-Isopropylthioxanthone (2-ITX) (CAS No 5495-84-1)	mg/kg	< 0.01	< 0.01
Ethyl-4-dimethylaminobenzoate (CAS No 10287-53-3)	mg/kg	0.73	0.74
2-Ethylhexyl-4-(dimethylamino)benzoate (CAS No 21245-02-3)	mg/kg	1.5	1.3
Phenylbis(2,4,6-trimethylbenzoyl)phosphin oxide (CAS No 162881-26-7)	mg/kg	< 0.01	< 0.01
Diphenyl-(2,4,6-trimethylbenzoyl)-phosphin oxide (CAS No 75980-60-8)	mg/kg	< 0.01	< 0.01
N-Phenylglycine (CAS No 103-01-5)	mg/kg	< 0.01	< 0.01
2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (CAS No 106797-53-9)	mg/kg	< 0.01	< 0.01
1-Hydroxycyclohexylphenylketone (CAS No 947-19-3)	mg/kg	3.0	4.6
2-Methyl-4'-(methylthio)-2-morpholinopropiophenone (CAS No 71868-10-5)	mg/kg	0.034	0.039
2-Benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone (CAS No 119313-12-1)	mg/kg	< 0.01	< 0.01

Parameter	Unit	17-084130-15	17-084130-16
4-(Dimethylamino)benzophenone (CAS No 530-44-9)	mg/kg	< 0.01	< 0.01
Leucomalachite green (CAS No 129-73-7)	mg/kg	< 0.01	< 0.01
Leucocrystal Violet (CAS No 603-48-5)		< 0.01	< 0.01
2,2-Diethoxyacetophenone (CAS No 6175-45-7)	mg/kg	< 0.01	< 0.01
4-Isopropylthioxanthone (4-ITX) (CAS No 83846-86-0)	mg/kg	< 0.01	< 0.01
Esacure one	mg/kg	< 0.01	< 0.01
2-Hydroxy-2-methylpropiophenon (CAS No 7473-98-5)	mg/kg	< 0.01	< 0.01
Esacure 1001 M (CAS No 272460-97-6)	mg/kg	< 0.01	< 0.01
Irgacure 250 (CAS No 344562-80-7)	mg/kg	< 0.01	< 0.01
Irgacure 379 (CAS No 119344-86-4)	mg/kg	< 0.01	< 0.01

Johannes Wächter
 (Food Chemist / Scientific Expert)

Report No. CAL17-134378-1/hve

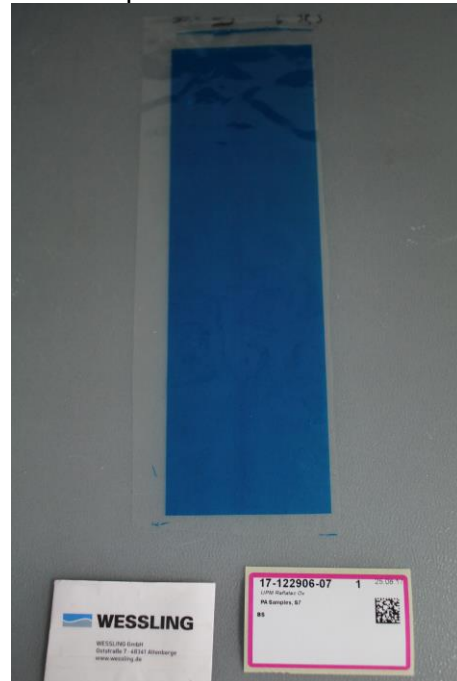
Altenberge, 3rd November 2017**Material testing**

- Sample receipt: 4th August / 17th August 2017
- Client: UPM Raflatac Oy, Tesomankatu 31,
33101 Tampere, Finland
- Order date: In written form dated 29th August 2017
- Sampled by: Client
- Beginning of examinations: 26th September 2017
- End of examinations: 2nd November 2017
- Sample No. 17-122906-02: Folie S2, PA
Sample No. 17-122906-07: Foile S7, PA
Sample No. 17-122906-11: Folie S11, clear PP
Sample No. 17-122906-14: Folie S14, clear PP
Sample No. 17-129374-04: Folie S22, very thin PET
Sample No. 17-129374-16: Folie S42, white PP
Sample No. 17-129374-19: Folie S45, white PP
Sample No. 17-129374-22: Folie S48, thin PET
Sample No. 17-129374-24: Folie S50, thin PET
Sample No. 17-129374-29: Folie S33, white PE
Sample No. 17-129374-30: Folie S35, thick white PP
Sample No. 17-129374-31: Folie S36, thick white PP
Sample No. 17-129374-33: Folie S34, white PE
Sample No. 17-129374-36: Folie S20, very thin PET
Sample No. 17-129374-43: Folie S59
Sample No. 17-129374-45: Folie S61
- Further information: -/-

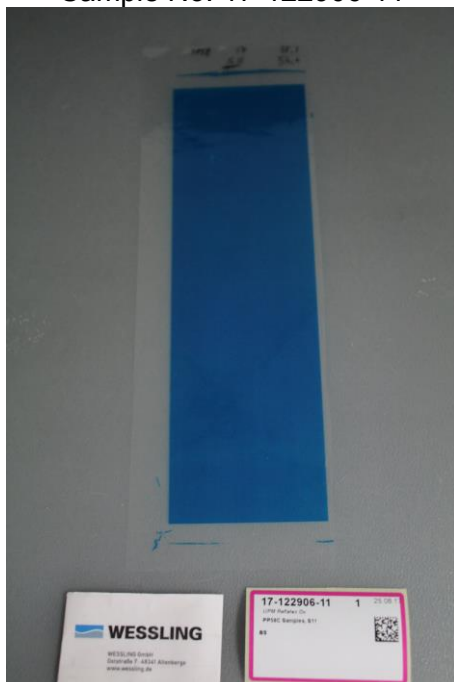
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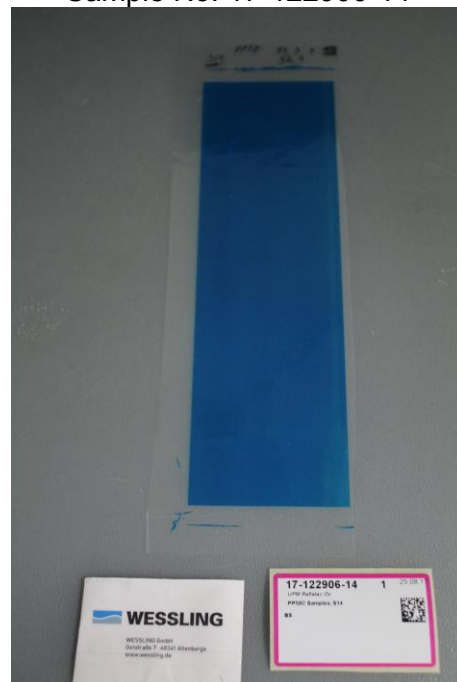
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Sample No. 17-122906-11



Sample No. 17-122906-14



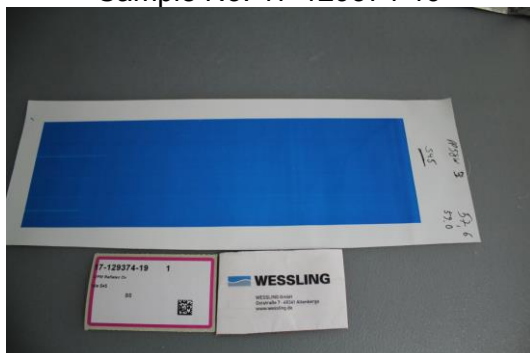
Sample No. 17-129374-04



Sample No. 17-129374-16



Sample No. 17-129374-19



Sample No. 17-129374-22



Sample No. 17-129374-24



Sample No. 17-129374-29



Sample No. 17-129374-30



Sample No. 17-129374-31



Sample No. 17-129374-33



Sample No. 17-129374-36



Sample No. 17-129374-43



Sample No. 17-129374-45



Analysed samples/parts:

Sample No.	Sample identifier
17-122906-02	Sample complete (food contact side)
17-122906-07	Sample complete (food contact side)
17-122906-11	Sample complete (food contact side)
17-122906-14	Sample complete (food contact side)
17-129374-04	Sample complete (food contact side)
17-129374-16	Sample complete (food contact side)
17-129374-19	Sample complete (food contact side)
17-129374-22	Sample complete (food contact side)
17-129374-24	Sample complete (food contact side)
17-129374-29	Sample complete (food contact side)
17-129374-30	Sample complete (food contact side)
17-129374-31	Sample complete (food contact side)
17-129374-33	Sample complete (food contact side)
17-129374-36	Sample complete (food contact side)
17-129374-43	Sample complete (food contact side)
17-129374-45	Sample complete (food contact side)

Examination methods:

Parameter	Method	Performing place
Preparation specific migration	DIN EN 13130-1 mod.	Produktanalytik Altenberge
Photoinitiators	WEX 217 (LC-MS/MS)	*

* tested by a cooperation laboratory

Results:

1. Photoinitiatoren / Photoinitiators

Prüfbedingungen / Test conditions:

 Isooctan / *Isooctane* 10 d, 40 °C O:V / S:V = 0,44 : 75 ml

Parameter / Parameter	Einheit Unit	17-122906-02 S2 PA	17-122906-07 S7 PA
Benzophenon / <i>Benzophenone</i> (CAS No 119-61-9)	mg/kg	< 0,1	< 0,1
2-Methylbenzophenon / <i>2-Methylbenzophenone</i> (CAS No 131-58-8)	mg/kg	< 0,01	< 0,01
4-Methylbenzophenon / <i>4-Methylbenzophenone</i> (CAS No 134-84-9)	mg/kg	< 0,01	< 0,01
Methyl-2-benzoylbenzoat / <i>Methyl-2-benzoylbenzoate</i> (CAS No 606-28-0)	mg/kg	< 0,01	< 0,01
4-Hydroxybenzophenon / <i>4-Hydroxybenzophenone</i> (CAS No 1137-42-4)	mg/kg	< 0,01	< 0,01
4-Phenylbenzophenon / <i>4-Phenylbenzophenone</i> (CAS No 2128-93-0)	mg/kg	< 0,01	< 0,01
4-Methoxybenzophenon / <i>4-Methoxybenzophenone</i> (CAS No 611-94-4)	mg/kg	< 0,01	< 0,01
Michlers Keton / <i>Michlers Ketone</i> (CAS No 90-94-8)	mg/kg	< 0,01	< 0,01
2-Carboxybenzophenon / <i>2-Carboxybenzophenone</i> (CAS No 85-52-9)	mg/kg	< 0,01	< 0,01
Michlers Ethylketon / <i>Michlers Ethylketone</i> (CAS No 90-93-7)	mg/kg	< 0,01	< 0,01
1-Chloro-4-propoxy-9H-thioxanthen-9-on / <i>1-Chloro-4-propoxy-9H-thioxanthen-9-one</i> (CPTX) (CAS No 142770-42-1)	mg/kg	< 0,01	< 0,01
2-Isopropylthioxanthon / <i>2-Isopropylthioxanthone</i> (ITX) (CAS No 5495-84-1)	mg/kg	< 0,01	< 0,01

Parameter / Parameter	Einheit Unit	17-122906-02 S2 PA	17-122906-07 S7 PA
Ethyl-4-dimethylaminobenzoat / <i>Ethyl-4-dimethylaminobenzoate</i> (CAS No 10287-53-3)	mg/kg	< 0,01	< 0,01
2-Ethylhexyl-4-(dimethylamino)benzoat / <i>2-Ethylhexyl-4-(dimethylamino)benzoate</i> (CAS No 21245-02-3)	mg/kg	< 0,01	< 0,01
Phenylbis(2,4,6-trimethylbenzoyl)phosphinoxid / <i>Phenylbis(2,4,6-trimethylbenzoyl)phosphin oxide</i> (CAS No 162881-26-7)	mg/kg	< 0,01	< 0,01
Diphenyl-(2,4,6-trimethylbenzoyl)-phosphinoxid / <i>Diphenyl-(2,4,6-trimethylbenzoyl)-phosphin oxide</i> (CAS No 75980-60-8)	mg/kg	< 0,01	< 0,01
N-Phenylglycin / <i>N-Phenylglycine</i> (CAS No 103-01-5)	mg/kg	< 0,01	< 0,01
2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiofenon / <i>2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiofenone</i> (CAS No 106797-53-9)	mg/kg	< 0,01	< 0,01
1-Hydroxycyclohexylphenylketon / <i>1-Hydroxycyclohexylphenylketone</i> (CAS No 947-19-3)	mg/kg	< 0,01	< 0,01
2-Methyl-4'-(Methylthio)-2-morpholinopropiophenon / <i>2-Methyl-4'-(Methylthio)-2-morpholinopropiophenone</i> (CAS No 71868-10-5)	mg/kg	< 0,01	< 0,01
2-Benzyl-2-(dimethylamino)-4'-morpholinobutyrophenon / <i>2-Benzyl-2-(dimethylamino)-4'-morpholino-butyrophenone</i> Irgacure 369 (CAS No 119313-12-1)	mg/kg	< 0,01	< 0,01
4-(Dimethylamino)benzophenone / <i>4-(Dimethylamino)benzophenone</i> (CAS No 530-44-9)	mg/kg	< 0,01	< 0,01
Leukomalachitgrün / <i>Leucomalachite green</i> CAS No 129-73-7)	mg/kg	< 0,01	< 0,01
2,4 Diethyl-9H-thioxanthen-9-on / <i>2,4 Diethyl-9H-thioxanthen-9-one</i> (DETX)	mg/kg	< 0,01	< 0,01

Parameter / Parameter	Einheit Unit	17-122906-02 S2 PA	17-122906-07 S7 PA
(CAS No 82799-44-8)			
2,2-Diethoxyacetophenon / 2,2-Diethoxyacetophenone (CAS No 6175-45-7)	mg/kg	< 0,01	< 0,01
Esacure 1001 M / Esacure 1001 M (CAS No 272460-97-6)	mg/kg	< 0,01	< 0,01
Leucocrystal Violet (CAS No 603-48-5)	mg/kg	< 0,01	< 0,01

Parameter / Parameter	Einheit Unit	17-122906-11 S11 clear PP	17-122906-14 S14 clear PP
Benzophenon / Benzophenone (CAS No 119-61-9)	mg/kg	< 0,1	< 0,1
2-Methylbenzophenon / 2-Methylbenzophenone (CAS No 131-58-8)	mg/kg	< 0,01	< 0,01
4-Methylbenzophenon / 4-Methylbenzophenone (CAS No 134-84-9)	mg/kg	< 0,01	< 0,01
Methyl-2-benzoylbenzoat / Methyl-2-benzoylbenzoate (CAS No 606-28-0)	mg/kg	2,3	2,4
4-Hydroxybenzophenon / 4-Hydroxybenzophenone (CAS No 1137-42-4)	mg/kg	< 0,01	< 0,01
4-Phenylbenzophenon / 4-Phenylbenzophenone (CAS No 2128-93-0)	mg/kg	0,66	0,72
4-Methoxybenzophenon / 4-Methoxybenzophenone (CAS No 611-94-4)	mg/kg	< 0,01	< 0,01
Michlers Keton / Michlers Ketone (CAS No 90-94-8)	mg/kg	< 0,01	< 0,01
2-Carboxybenzophenon / 2-Carboxybenzophenone (CAS No 85-52-9)	mg/kg	< 0,01	< 0,01
Michlers Ethylketon / Michlers Ethylke- tone (CAS No 90-93-7)	mg/kg	< 0,01	< 0,01
1-Chloro-4-propoxy-9H-thioxanthen-9- on / 1-Chloro-4-propoxy-9H- thioxanthen-9-one (CPTX) (CAS No 142770-42-1)	mg/kg	< 0,01	< 0,01

Parameter / Parameter	Einheit Unit	17-122906-11 S11 clear PP	17-122906-14 S14 clear PP
2-Isopropylthioxanthon / 2-Isopropylthioxanthone (ITX) (CAS No 5495-84-1)	mg/kg	< 0,01	< 0,01
Ethyl-4-dimethylaminobenzoat / Ethyl- 4-dimethylaminobenzoate (CAS No 10287-53-3)	mg/kg	0,043	0,045
2-Ethylhexyl-4-(dimethylamino)benzoat / 2-Ethylhexyl-4- (dimethylamino)benzoate (CAS No 21245-02-3)	mg/kg	0,052	0,045
Phenylbis(2,4,6- trimethylbenzoyl)phosphinoxid / Phenylbis(2,4,6- trimethylbenzoyl)phosphin oxide (CAS No 162881-26-7)	mg/kg	< 0,01	< 0,01
Diphenyl-(2,4,6-trimethylbenzoyl)- phosphinoxid / Diphenyl-(2,4,6- trimethylbenzoyl)-phosphin oxide (CAS No 75980-60-8)	mg/kg	< 0,01	< 0,01
N-Phenylglycin / N-Phenylglycine (CAS No 103-01-5)	mg/kg	< 0,01	< 0,01
2-Hydroxy-4'-(2-hydroxyethoxy)-2- methylpropiofenon / 2-Hydroxy-4'-(2-hydroxyethoxy)-2- methylpropiofenone (CAS No 106797-53-9)	mg/kg	< 0,01	< 0,01
1-Hydroxycyclohexylphenylketon / 1-Hydroxycyclohexylphenylketone (CAS No 947-19-3)	mg/kg	0,67	0,80
2-Methyl-4'-(Methylthio)-2- morpholinopropiophenon / 2-Methyl-4'-(Methylthio)-2- morpholinopropiophenone (CAS No 71868-10-5)	mg/kg	< 0,01	0,012
2-Benzyl-2-(dimethylamino)-4'- morpholinobutyrophenon / 2-Benzyl-2-(dimethylamino)-4'- morpholino-butyrophenone Irgacure 369 (CAS No 119313-12-1)	mg/kg	< 0,01	< 0,01
4-(Dimethylamino)benzophenone / 4- (Dimethylamino)benzophenone (CAS No 530-44-9)	mg/kg	< 0,01	< 0,01

Parameter / Parameter	Einheit Unit	17-122906-11 S11 clear PP	17-122906-14 S14 clear PP
Leukomalachitgrün / <i>Leucomalachite green</i> CAS No 129-73-7)	mg/kg	< 0,01	< 0,01
2,4 Diethyl-9H-thioxanthen-9-on / 2,4 <i>Diethyl-9H-thioxanthen-9-one</i> (DETX) (CAS No 82799-44-8)	mg/kg	0,067	0,065
2,2-Diethoxyacetophenon / <i>2,2-Diethoxyacetophenone</i> (CAS No 6175-45-7)	mg/kg	< 0,01	< 0,01
Esacure 1001 M / <i>Esacure 1001 M</i> (CAS No 272460-97-6)	mg/kg	< 0,01	< 0,01
Leucocrystal Violet (CAS No 603-48-5)	mg/kg	< 0,01	< 0,01

Parameter / Parameter	Einheit Unit	17-129374-04 S22 very thin PET	17-129374-16 S42 white PP
Benzophenon / <i>Benzophenone</i> (CAS No 119-61-9)	mg/kg	< 0,1	< 0,1
2-Methylbenzophenon / <i>2-Methylbenzophenone</i> (CAS No 131-58-8)	mg/kg	< 0,01	< 0,01
4-Methylbenzophenon / <i>4-Methylbenzophenone</i> (CAS No 134-84-9)	mg/kg	< 0,01	< 0,01
Methyl-2-benzoylbenzoat / <i>Methyl-2-benzoylbenzoate</i> (CAS No 606-28-0)	mg/kg	< 0,01	2,0
4-Hydroxybenzophenon / <i>4-Hydroxybenzophenone</i> (CAS No 1137-42-4)	mg/kg	< 0,01	< 0,01
4-Phenylbenzophenon / <i>4-Phenylbenzophenone</i> (CAS No 2128-93-0)	mg/kg	< 0,01	0,51
4-Methoxybenzophenon / <i>4-Methoxybenzophenone</i> (CAS No 611-94-4)	mg/kg	< 0,01	< 0,01
Michlers Keton / <i>Michlers Ketone</i> (CAS No 90-94-8)	mg/kg	< 0,01	< 0,01
2-Carboxybenzophenon / <i>2-Carboxybenzophenone</i> (CAS No 85-52-9)	mg/kg	< 0,01	< 0,01

Parameter / Parameter	Einheit Unit	17-129374-04 S22 very thin PET	17-129374-16 S42 white PP
Michlers Ethylketon / <i>Michlers Ethylketone</i> (CAS No 90-93-7)	mg/kg	< 0,01	< 0,01
1-Chloro-4-propoxy-9H-thioxanthen-9-on / <i>1-Chloro-4-propoxy-9H-thioxanthen-9-one</i> (CPTX) (CAS No 142770-42-1)	mg/kg	< 0,01	< 0,01
2-Isopropylthioxanthon / <i>2-Isopropylthioxanthone</i> (ITX) (CAS No 5495-84-1)	mg/kg	< 0,01	< 0,01
Ethyl-4-dimethylaminobenzoat / <i>Ethyl-4-dimethylaminobenzoate</i> (CAS No 10287-53-3)	mg/kg	< 0,01	0,023
2-Ethylhexyl-4-(dimethylamino)benzoat / <i>2-Ethylhexyl-4-(dimethylamino)benzoate</i> (CAS No 21245-02-3)	mg/kg	< 0,01	0,020
Phenylbis(2,4,6-trimethylbenzoyl)phosphinoxid / <i>Phenylbis(2,4,6-trimethylbenzoyl)phosphin oxide</i> (CAS No 162881-26-7)	mg/kg	< 0,01	< 0,01
Diphenyl-(2,4,6-trimethylbenzoyl)-phosphinoxid / <i>Diphenyl-(2,4,6-trimethylbenzoyl)-phosphin oxide</i> (CAS No 75980-60-8)	mg/kg	< 0,01	< 0,01
N-Phenylglycin / <i>N-Phenylglycine</i> (CAS No 103-01-5)	mg/kg	< 0,01	< 0,01
2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenon / <i>2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone</i> (CAS No 106797-53-9)	mg/kg	< 0,01	< 0,01
1-Hydroxycyclohexylphenylketon / <i>1-Hydroxycyclohexylphenylketone</i> (CAS No 947-19-3)	mg/kg	< 0,01	0,53
2-Methyl-4'-(Methylthio)-2-morpholinopropiophenon / <i>2-Methyl-4'-(Methylthio)-2-morpholinopropiophenone</i> (CAS No 71868-10-5)	mg/kg	< 0,01	< 0,01

Parameter / Parameter	Einheit Unit	17-129374-04 S22 very thin PET	17-129374-16 S42 white PP
2-Benzyl-2-(dimethylamino)-4'-morpholinobutyrophenon / 2-Benzyl-2-(dimethylamino)-4'-morpholino-butyrophenone Irgacure 369 (CAS No 119313-12-1)	mg/kg	< 0,01	< 0,01
4-(Dimethylamino)benzophenone / 4-(Dimethylamino)benzophenone (CAS No 530-44-9)	mg/kg	< 0,01	< 0,01
Leukomalachitgrün / Leucomalachite green CAS No 129-73-7)	mg/kg	< 0,01	< 0,01
2,4 Diethyl-9H-thioxanthen-9-on / 2,4 Diethyl-9H-thioxanthen-9-one (DETX) (CAS No 82799-44-8)	mg/kg	< 0,01	0,024
2,2-Diethoxyacetophenon / 2,2-Diethoxyacetophenone (CAS No 6175-45-7)	mg/kg	< 0,01	< 0,01
Esacure 1001 M / Esacure 1001 M (CAS No 272460-97-6)	mg/kg	< 0,01	< 0,01
Leucocrystal Violet (CAS No 603-48-5)	mg/kg	< 0,01	< 0,01

Parameter / Parameter	Einheit Unit	17-129374-19 S19 white PP	17-129374-22 S48 thin PET
Benzophenon / Benzophenone (CAS No 119-61-9)	mg/kg	< 0,1	< 0,1
2-Methylbenzophenon / 2-Methylbenzophenone (CAS No 131-58-8)	mg/kg	< 0,01	< 0,01
4-Methylbenzophenon / 4-Methylbenzophenone (CAS No 134-84-9)	mg/kg	< 0,01	< 0,01
Methyl-2-benzoylbenzoat / Methyl-2-benzoylbenzoate (CAS No 606-28-0)	mg/kg	2,1	< 0,01
4-Hydroxybenzophenon / 4-Hydroxybenzophenone (CAS No 1137-42-4)	mg/kg	< 0,01	< 0,01
4-Phenylbenzophenon / 4-Phenylbenzophenone (CAS No 2128-93-0)	mg/kg	0,63	< 0,01

Parameter / <i>Parameter</i>	Einheit <i>Unit</i>	17-129374-19 S19 white PP	17-129374-22 S48 thin PET
4-Methoxybenzophenon / <i>4-Methoxybenzophenone</i> (CAS No 611-94-4)	mg/kg	< 0,01	< 0,01
Michlers Keton / <i>Michlers Ketone</i> (CAS No 90-94-8)	mg/kg	< 0,01	< 0,01
2-Carboxybenzophenon / <i>2-Carboxybenzophenone</i> (CAS No 85-52-9)	mg/kg	< 0,01	< 0,01
Michlers Ethylketon / <i>Michlers Ethylke- tone</i> (CAS No 90-93-7)	mg/kg	< 0,01	< 0,01
1-Chloro-4-propoxy-9H-thioxanthen-9- on / <i>1-Chloro-4-propoxy-9H- thioxanthen-9-one</i> (CPTX) (CAS No 142770-42-1)	mg/kg	< 0,01	< 0,01
2-Isopropylthioxanthon / <i>2-Isopropylthioxanthone</i> (ITX) (CAS No 5495-84-1)	mg/kg	< 0,01	< 0,01
Ethyl-4-dimethylaminobenzoat / <i>Ethyl- 4-dimethylaminobenzoate</i> (CAS No 10287-53-3)	mg/kg	0,032	< 0,01
2-Ethylhexyl-4-(dimethylamino)benzoat / <i>2-Ethylhexyl-4- (dimethylamino)benzoate</i> (CAS No 21245-02-3)	mg/kg	0,022	< 0,01
Phenylbis(2,4,6- trimethylbenzoyl)phosphinoxid / <i>Phenylbis(2,4,6- trimethylbenzoyl)phosphinoxide</i> (CAS No 162881-26-7)	mg/kg	< 0,01	< 0,01
Diphenyl-(2,4,6-trimethylbenzoyl)- phosphinoxid / <i>Diphenyl-(2,4,6- trimethylbenzoyl)-phosphinoxide</i> (CAS No 75980-60-8)	mg/kg	< 0,01	< 0,01
N-Phenylglycin / <i>N-Phenylglycine</i> (CAS No 103-01-5)	mg/kg	< 0,01	< 0,01
2-Hydroxy-4'-(2-hydroxyethoxy)-2- methylpropiophenon / <i>2-Hydroxy-4'-(2-hydroxyethoxy)-2- methylpropiophenone</i> (CAS No 106797-53-9)	mg/kg	< 0,01	< 0,01
1-Hydroxycyclohexylphenylketon / <i>1-Hydroxycyclohexylphenylketone</i> (CAS No 947-19-3)	mg/kg	0,61	< 0,01

Parameter / Parameter	Einheit Unit	17-129374-19 S19 white PP	17-129374-22 S48 thin PET
2-Methyl-4'-(Methylthio)-2-morpholinopropiophenon / 2-Methyl-4'-(Methylthio)-2-morpholinopropiophenone (CAS No 71868-10-5)	mg/kg	< 0,01	< 0,01
2-Benzyl-2-(dimethylamino)-4'-morpholinobutyrophenon / 2-Benzyl-2-(dimethylamino)-4'-morpholino-butyrophenone Irgacure 369 (CAS No 119313-12-1)	mg/kg	< 0,01	< 0,01
4-(Dimethylamino)benzophenone / 4-(Dimethylamino)benzophenone (CAS No 530-44-9)	mg/kg	< 0,01	< 0,01
Leukomalachitgrün / Leucomalachite green CAS No 129-73-7)	mg/kg	< 0,01	< 0,01
2,4 Diethyl-9H-thioxanthen-9-on / 2,4 Diethyl-9H-thioxanthen-9-one (DETX) (CAS No 82799-44-8)	mg/kg	0,024	< 0,01
2,2-Diethoxyacetophenon / 2,2-Diethoxyacetophenone (CAS No 6175-45-7)	mg/kg	< 0,01	< 0,01
Esacure 1001 M / Esacure 1001 M (CAS No 272460-97-6)	mg/kg	< 0,01	< 0,01
Leucocrystal Violet (CAS No 603-48-5)	mg/kg	< 0,01	< 0,01

Parameter / Parameter	Einheit Unit	17-129374-24 S50 thin PET	17-129374-29 S33 white PE
Benzophenon / Benzophenone (CAS No 119-61-9)	mg/kg	< 0,1	< 0,1
2-Methylbenzophenon / 2-Methylbenzophenone (CAS No 131-58-8)	mg/kg	< 0,01	< 0,01
4-Methylbenzophenon / 4-Methylbenzophenone (CAS No 134-84-9)	mg/kg	< 0,01	< 0,01
Methyl-2-benzoylbenzoat / Methyl-2-benzoylbenzoate (CAS No 606-28-0)	mg/kg	< 0,01	2,2

Parameter / Parameter	Einheit Unit	17-129374-24 S50 thin PET	17-129374-29 S33 white PE
4-Hydroxybenzophenon / 4-Hydroxybenzophenone (CAS No 1137-42-4)	mg/kg	< 0,01	< 0,01
4-Phenylbenzophenon / 4-Phenylbenzophenone (CAS No 2128-93-0)	mg/kg	< 0,01	0,72
4-Methoxybenzophenon / 4-Methoxybenzophenone (CAS No 611-94-4)	mg/kg	< 0,01	< 0,01
Michlers Keton / Michlers Ketone (CAS No 90-94-8)	mg/kg	< 0,01	< 0,01
2-Carboxybenzophenon / 2-Carboxybenzophenone (CAS No 85-52-9)	mg/kg	< 0,01	< 0,01
Michlers Ethylketon / Michlers Ethylke- tone (CAS No 90-93-7)	mg/kg	< 0,01	< 0,01
1-Chloro-4-propoxy-9H-thioxanthen-9- on / 1-Chloro-4-propoxy-9H- thioxanthen-9-one (CPTX) (CAS No 142770-42-1)	mg/kg	< 0,01	< 0,01
2-Isopropylthioxanthon / 2-Isopropylthioxanthone (ITX) (CAS No 5495-84-1)	mg/kg	< 0,01	< 0,01
Ethyl-4-dimethylaminobenzoat / Ethyl- 4-dimethylaminobenzoate (CAS No 10287-53-3)	mg/kg	< 0,01	0,033
2-Ethylhexyl-4-(dimethylamino)benzoat / 2-Ethylhexyl-4- (dimethylamino)benzoate (CAS No 21245-02-3)	mg/kg	< 0,01	0,029
Phenylbis(2,4,6- trimethylbenzoyl)phosphinoxid / Phenylbis(2,4,6- trimethylbenzoyl)phosphin oxide (CAS No 162881-26-7)	mg/kg	< 0,01	< 0,01
Diphenyl-(2,4,6-trimethylbenzoyl)- phosphinoxid / Diphenyl-(2,4,6- trimethylbenzoyl)-phosphin oxide (CAS No 75980-60-8)	mg/kg	< 0,01	< 0,01
N-Phenylglycin / N-Phenylglycine (CAS No 103-01-5)	mg/kg	< 0,01	< 0,01

Parameter / Parameter	Einheit Unit	17-129374-24 S50 thin PET	17-129374-29 S33 white PE
2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenon / 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (CAS No 106797-53-9)	mg/kg	< 0,01	< 0,01
1-Hydroxycyclohexylphenylketon / 1-Hydroxycyclohexylphenylketone (CAS No 947-19-3)	mg/kg	< 0,01	0,55
2-Methyl-4'-(Methylthio)-2-morpholinopropiophenon / 2-Methyl-4'-(Methylthio)-2-morpholinopropiophenone (CAS No 71868-10-5)	mg/kg	< 0,01	< 0,01
2-Benzyl-2-(dimethylamino)-4'-morpholinobutyrophenon / 2-Benzyl-2-(dimethylamino)-4'-morpholino-butyrophenone Irgacure 369 (CAS No 119313-12-1)	mg/kg	< 0,01	< 0,01
4-(Dimethylamino)benzophenone / 4-(Dimethylamino)benzophenone (CAS No 530-44-9)	mg/kg	< 0,01	< 0,01
Leukomalachitgrün / Leucomalachite green (CAS No 129-73-7)	mg/kg	< 0,01	< 0,01
2,4 Diethyl-9H-thioxanthen-9-on / 2,4 Diethyl-9H-thioxanthen-9-one (DETX) (CAS No 82799-44-8)	mg/kg	< 0,01	0,041
2,2-Diethoxyacetophenon / 2,2-Diethoxyacetophenone (CAS No 6175-45-7)	mg/kg	< 0,01	< 0,01
Esacure 1001 M / Esacure 1001 M (CAS No 272460-97-6)	mg/kg	< 0,01	< 0,01
Leucocrystal Violet (CAS No 603-48-5)	mg/kg	< 0,01	< 0,01

Parameter / Parameter	Einheit Unit	17-129374-30 S35 thick white PP	17-129374-31 S36 thick white PP
Benzophenon / Benzophenone (CAS No 119-61-9)	mg/kg	< 0,1	< 0,1

Parameter / <i>Parameter</i>	Einheit <i>Unit</i>	17-129374-30 S35 thick white PP	17-129374-31 S36 thick white PP
2-Methylbenzophenon / <i>2-Methylbenzophenone</i> (CAS No 131-58-8)	mg/kg	< 0,01	< 0,01
4-Methylbenzophenon / <i>4-Methylbenzophenone</i> (CAS No 134-84-9)	mg/kg	< 0,01	< 0,01
Methyl-2-benzoylbenzoat / <i>Methyl-2-benzoylbenzoate</i> (CAS No 606-28-0)	mg/kg	3,0	2,7
4-Hydroxybenzophenon / <i>4-Hydroxybenzophenone</i> (CAS No 1137-42-4)	mg/kg	< 0,01	< 0,01
4-Phenylbenzophenon / <i>4-Phenylbenzophenone</i> (CAS No 2128-93-0)	mg/kg	0,78	0,68
4-Methoxybenzophenon / <i>4-Methoxybenzophenone</i> (CAS No 611-94-4)	mg/kg	< 0,01	< 0,01
Michlers Keton / <i>Michlers Ketone</i> (CAS No 90-94-8)	mg/kg	< 0,01	< 0,01
2-Carboxybenzophenon / <i>2-Carboxybenzophenone</i> (CAS No 85-52-9)	mg/kg	< 0,01	< 0,01
Michlers Ethylketon / <i>Michlers Ethylke- tone</i> (CAS No 90-93-7)	mg/kg	< 0,01	< 0,01
1-Chloro-4-propoxy-9H-thioxanthen-9- on / <i>1-Chloro-4-propoxy-9H- thioxanthen-9-one</i> (CPTX) (CAS No 142770-42-1)	mg/kg	< 0,01	< 0,01
2-Isopropylthioxanthon / <i>2-Isopropylthioxanthone</i> (ITX) (CAS No 5495-84-1)	mg/kg	< 0,01	< 0,01
Ethyl-4-dimethylaminobenzoat / <i>Ethyl- 4-dimethylaminobenzoate</i> (CAS No 10287-53-3)	mg/kg	0,031	0,031
2-Ethylhexyl-4-(dimethylamino)benzoat / <i>2-Ethylhexyl-4- (dimethylamino)benzoate</i> (CAS No 21245-02-3)	mg/kg	0,015	0,018

Parameter / <i>Parameter</i>	Einheit <i>Unit</i>	17-129374-30 S35 thick white PP	17-129374-31 S36 thick white PP
Phenylbis(2,4,6-trimethylbenzoyl)phosphinoxid / <i>Phenylbis(2,4,6-trimethylbenzoyl)phosphin oxide</i> (CAS No 162881-26-7)	mg/kg	< 0,01	< 0,01
Diphenyl-(2,4,6-trimethylbenzoyl)-phosphinoxid / <i>Diphenyl-(2,4,6-trimethylbenzoyl)-phosphin oxide</i> (CAS No 75980-60-8)	mg/kg	< 0,01	< 0,01
N-Phenylglycin / <i>N-Phenylglycine</i> (CAS No 103-01-5)	mg/kg	< 0,01	< 0,01
2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenon / <i>2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone</i> (CAS No 106797-53-9)	mg/kg	< 0,01	< 0,01
1-Hydroxycyclohexylphenylketon / <i>1-Hydroxycyclohexylphenylketone</i> (CAS No 947-19-3)	mg/kg	0,66	0,71
2-Methyl-4'-(Methylthio)-2-morpholinopropiophenon / <i>2-Methyl-4'-(Methylthio)-2-morpholinopropiophenone</i> (CAS No 71868-10-5)	mg/kg	< 0,01	< 0,01
2-Benzyl-2-(dimethylamino)-4'-morpholinobutyrophenon / <i>2-Benzyl-2-(dimethylamino)-4'-morpholino-butyrophenone</i> Irgacure 369 (CAS No 119313-12-1)	mg/kg	< 0,01	< 0,01
4-(Dimethylamino)benzophenone / <i>4-(Dimethylamino)benzophenone</i> (CAS No 530-44-9)	mg/kg	< 0,01	< 0,01
Leukomalachitgrün / <i>Leucomalachite green</i> (CAS No 129-73-7)	mg/kg	< 0,01	< 0,01
2,4 Diethyl-9H-thioxanthen-9-on / <i>2,4 Diethyl-9H-thioxanthen-9-one</i> (DETX) (CAS No 82799-44-8)	mg/kg	0,015	0,017
2,2-Diethoxyacetophenon / <i>2,2-Diethoxyacetophenone</i> (CAS No 6175-45-7)	mg/kg	< 0,01	< 0,01
Esacure 1001 M / <i>Esacure 1001 M</i> (CAS No 272460-97-6)	mg/kg	< 0,01	< 0,01

Parameter / <i>Parameter</i>	Einheit <i>Unit</i>	17-129374-30 S35 thick white PP	17-129374-31 S36 thick white PP
Leucocrystal Violet (CAS No 603-48-5)	mg/kg	< 0,01	< 0,01

Parameter / <i>Parameter</i>	Einheit <i>Unit</i>	17-129374-33 S34 white PE	17-129374-36 S20 very thin PET
Benzophenon / <i>Benzophenone</i> (CAS No 119-61-9)	mg/kg	< 0,1	< 0,1
2-Methylbenzophenon / <i>2-Methylbenzophenone</i> (CAS No 131-58-8)	mg/kg	< 0,01	< 0,01
4-Methylbenzophenon / <i>4-Methylbenzophenone</i> (CAS No 134-84-9)	mg/kg	< 0,01	< 0,01
Methyl-2-benzoylbenzoat / <i>Methyl-2-benzoylbenzoate</i> (CAS No 606-28-0)	mg/kg	2,1	1,2
4-Hydroxybenzophenon / <i>4-Hydroxybenzophenone</i> (CAS No 1137-42-4)	mg/kg	< 0,01	< 0,01
4-Phenylbenzophenon / <i>4-Phenylbenzophenone</i> (CAS No 2128-93-0)	mg/kg	0,61	0,54
4-Methoxybenzophenon / <i>4-Methoxybenzophenone</i> (CAS No 611-94-4)	mg/kg	< 0,01	< 0,01
Michlers Keton / <i>Michlers Ketone</i> (CAS No 90-94-8)	mg/kg	< 0,01	< 0,01
2-Carboxybenzophenon / <i>2-Carboxybenzophenone</i> (CAS No 85-52-9)	mg/kg	< 0,01	< 0,01
Michlers Ethylketon / <i>Michlers Ethylke- tone</i> (CAS No 90-93-7)	mg/kg	< 0,01	< 0,01
1-Chloro-4-propoxy-9H-thioxanthen-9- on / <i>1-Chloro-4-propoxy-9H- thioxanthen-9-one</i> (CPTX) (CAS No 142770-42-1)	mg/kg	< 0,01	< 0,01
2-Isopropylthioxanthon / <i>2-Isopropylthioxanthone</i> (ITX) (CAS No 5495-84-1)	mg/kg	< 0,01	< 0,01

Parameter / <i>Parameter</i>	Einheit <i>Unit</i>	17-129374-33 S34 white PE	17-129374-36 S20 very thin PET
Ethyl-4-dimethylaminobenzoat / <i>Ethyl-4-dimethylaminobenzoate</i> (CAS No 10287-53-3)	mg/kg	0,045	0,019
2-Ethylhexyl-4-(dimethylamino)benzoat / <i>2-Ethylhexyl-4-(dimethylamino)benzoate</i> (CAS No 21245-02-3)	mg/kg	0,027	0,013
Phenylbis(2,4,6-trimethylbenzoyl)phosphinoxid / <i>Phenylbis(2,4,6-trimethylbenzoyl)phosphin oxide</i> (CAS No 162881-26-7)	mg/kg	< 0,01	< 0,01
Diphenyl-(2,4,6-trimethylbenzoyl)-phosphinoxid / <i>Diphenyl-(2,4,6-trimethylbenzoyl)-phosphin oxide</i> (CAS No 75980-60-8)	mg/kg	< 0,01	< 0,01
N-Phenylglycin / <i>N-Phenylglycine</i> (CAS No 103-01-5)	mg/kg	< 0,01	< 0,01
2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiofenon / <i>2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiofenone</i> (CAS No 106797-53-9)	mg/kg	< 0,01	< 0,01
1-Hydroxycyclohexylphenylketon / <i>1-Hydroxycyclohexylphenylketone</i> (CAS No 947-19-3)	mg/kg	0,62	0,58
2-Methyl-4'-(Methylthio)-2-morpholinopropiofenon / <i>2-Methyl-4'-(Methylthio)-2-morpholinopropiofenone</i> (CAS No 71868-10-5)	mg/kg	< 0,01	< 0,01
2-Benzyl-2-(dimethylamino)-4'-morpholinobutyrophenon / <i>2-Benzyl-2-(dimethylamino)-4'-morpholino-butyrophenone</i> Irgacure 369 (CAS No 119313-12-1)	mg/kg	< 0,01	< 0,01
4-(Dimethylamino)benzophenon / <i>4-(Dimethylamino)benzophenone</i> (CAS No 530-44-9)	mg/kg	< 0,01	< 0,01
Leukomalachitgrün / <i>Leucomalachite green</i> (CAS No 129-73-7)	mg/kg	< 0,01	< 0,01

Parameter / Parameter	Einheit Unit	17-129374-33 S34 white PE	17-129374-36 S20 very thin PET
2,4 Diethyl-9H-thioxanthen-9-on / 2,4 <i>Diethyl-9H-thioxanthen-9-one</i> (DETX) (CAS No 82799-44-8)	mg/kg	0,038	0,026
2,2-Diethoxyacetophenon / <i>2,2-Diethoxyacetophenone</i> (CAS No 6175-45-7)	mg/kg	< 0,01	< 0,01
Esacure 1001 M / <i>Esacure 1001 M</i> (CAS No 272460-97-6)	mg/kg	< 0,01	< 0,01
Leucocrystal Violet (CAS No 603-48-5)	mg/kg	< 0,01	< 0,01

Parameter / Parameter	Einheit Unit	17-129374-43 S59	17-129374-45 S61
Benzophenon / <i>Benzophenone</i> (CAS No 119-61-9)	mg/kg	< 0,1	< 0,1
2-Methylbenzophenon / <i>2-Methylbenzophenone</i> (CAS No 131-58-8)	mg/kg	< 0,01	< 0,01
4-Methylbenzophenon / <i>4-Methylbenzophenone</i> (CAS No 134-84-9)	mg/kg	< 0,01	< 0,01
Methyl-2-benzoylbenzoat / <i>Methyl-2-benzoylbenzoate</i> (CAS No 606-28-0)	mg/kg	2,3	2,4
4-Hydroxybenzophenon / <i>4-Hydroxybenzophenone</i> (CAS No 1137-42-4)	mg/kg	< 0,01	< 0,01
4-Phenylbenzophenon / <i>4-Phenylbenzophenone</i> (CAS No 2128-93-0)	mg/kg	0,82	0,76
4-Methoxybenzophenon / <i>4-Methoxybenzophenone</i> (CAS No 611-94-4)	mg/kg	< 0,01	< 0,01
Michlers Keton / <i>Michlers Ketone</i> (CAS No 90-94-8)	mg/kg	< 0,01	< 0,01
2-Carboxybenzophenon / <i>2-Carboxybenzophenone</i> (CAS No 85-52-9)	mg/kg	< 0,01	< 0,01

Parameter / Parameter	Einheit Unit	17-129374-43 S59	17-129374-45 S61
Michlers Ethylketon / <i>Michlers Ethylketone</i> (CAS No 90-93-7)	mg/kg	< 0,01	< 0,01
1-Chloro-4-propoxy-9H-thioxanthen-9-on / <i>1-Chloro-4-propoxy-9H-thioxanthen-9-one</i> (CPTX) (CAS No 142770-42-1)	mg/kg	< 0,01	< 0,01
2-Isopropylthioxanthon / <i>2-Isopropylthioxanthone</i> (ITX) (CAS No 5495-84-1)	mg/kg	< 0,01	< 0,01
Ethyl-4-dimethylaminobenzoat / <i>Ethyl-4-dimethylaminobenzoate</i> (CAS No 10287-53-3)	mg/kg	0,16	0,07
2-Ethylhexyl-4-(dimethylamino)benzoat / <i>2-Ethylhexyl-4-(dimethylamino)benzoate</i> (CAS No 21245-02-3)	mg/kg	0,035	0,033
Phenylbis(2,4,6-trimethylbenzoyl)phosphinoxid / <i>Phenylbis(2,4,6-trimethylbenzoyl)phosphin oxide</i> (CAS No 162881-26-7)	mg/kg	< 0,01	< 0,01
Diphenyl-(2,4,6-trimethylbenzoyl)-phosphinoxid / <i>Diphenyl-(2,4,6-trimethylbenzoyl)-phosphin oxide</i> (CAS No 75980-60-8)	mg/kg	< 0,01	< 0,01
N-Phenylglycin / <i>N-Phenylglycine</i> (CAS No 103-01-5)	mg/kg	< 0,01	< 0,01
2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenon / <i>2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone</i> (CAS No 106797-53-9)	mg/kg	< 0,01	< 0,01
1-Hydroxycyclohexylphenylketon / <i>1-Hydroxycyclohexylphenylketone</i> (CAS No 947-19-3)	mg/kg	0,80	0,67
2-Methyl-4'-(Methylthio)-2-morpholinopropiophenon / <i>2-Methyl-4'-(Methylthio)-2-morpholinopropiophenone</i> (CAS No 71868-10-5)	mg/kg	0,012	< 0,01

Parameter / Parameter	Einheit Unit	17-129374-43 S59	17-129374-45 S61
2-Benzyl-2-(dimethylamino)-4'-morpholinobutyrophenon / 2-Benzyl-2-(dimethylamino)-4'-morpholino-butyrophenone Irgacure 369 (CAS No 119313-12-1)	mg/kg	0,013	< 0,01
4-(Dimethylamino)benzophenone / 4-(Dimethylamino)benzophenone (CAS No 530-44-9)	mg/kg	< 0,01	< 0,01
Leukomalachitgrün / Leucomalachite green CAS No 129-73-7)	mg/kg	< 0,01	< 0,01
2,4 Diethyl-9H-thioxanthen-9-on / 2,4 Diethyl-9H-thioxanthen-9-one (DETX) (CAS No 82799-44-8)	mg/kg	0,42	0,040
2,2-Diethoxyacetophenon / 2,2-Diethoxyacetophenone (CAS No 6175-45-7)	mg/kg	< 0,01	< 0,01
Esacure 1001 M / Esacure 1001 M (CAS No 272460-97-6)	mg/kg	< 0,01	< 0,01
Leucocrystal Violet (CAS No 603-48-5)	mg/kg	< 0,01	< 0,01

Johannes Wächter
 (Food Chemist / Scientific Expert)

Report No. CAL17-145953-1/hve

Altenberge, 27th November 2017**Material testing**

- Sample receipt: 4th August / 17th August 2017
- Client: UPM Raflatac Oy, Tesomankatu 31,
33101 Tampere, Finland
- Order date: In written form dated 29th August 2017
- Sampled by: Client
- Beginning of examinations: 25th October 2017
- End of examinations: 23rd November 2017
- Sample No. 17-122906-04: Folie S4, (polyamide)
Sample No. 17-122906-05: Folie S5 (polyamide)
Sample No. 17-122906-09: Folie S9, (clear PP)
Sample No. 17-122906-12: Folie S12, (clear PP)
Sample No. 17-129374-02: Folie S19 (very thin PP)
Sample No. 17-129374-07: Folie S25 (clear PE)
Sample No. 17-129374-08: Folie S26 (clear PE)p
Sample No. 17-129374-13: Folie S39 (thick white PE)
Sample No. 17-129374-14: Folie S40 (thick white PE)
Sample No. 17-129374-17: Folie S43 (white PP)
Sample No. 17-129374-18: Folie S44 (white PP)
Sample No. 17-129374-23: Folie S49 (thin PET)
Sample No. 17-129374-25: Folie S51 (thin PET)
Sample No. 17-129374-27: Folie S31 (white PE)
Sample No. 17-129374-28: Folie S32 (white PE)
Sample No. 17-129374-35: Folie S17 (very thin PP)
Sample No. 17-129374-37: Folie S53 (PET)
Sample No. 17-129374-39: Folie S55 (PET)
Sample No. 17-129374-41: Folie S57 (white thick PE)
Sample No. 17-129374-44: Folie S60 (white thick PE)
- Further information: -/-

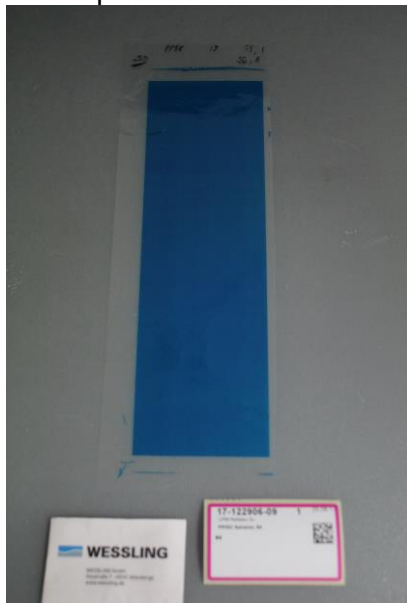
Sample No. 17-122906-04



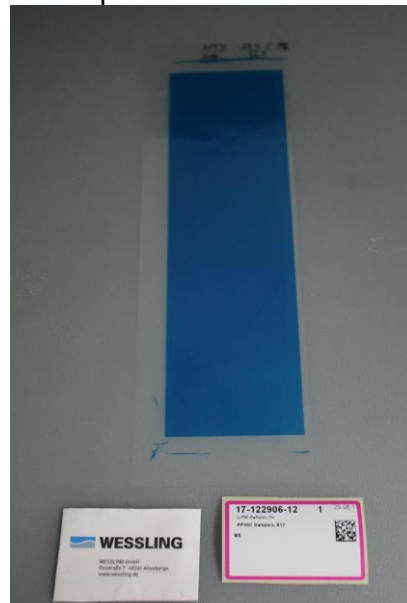
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Sample No. 17-122906-09



Sample No. 17-122906-12



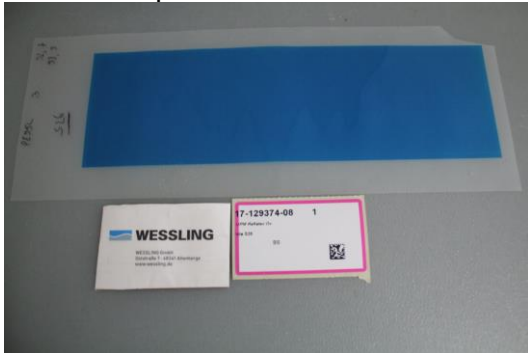
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Sample No. 17-129374-07



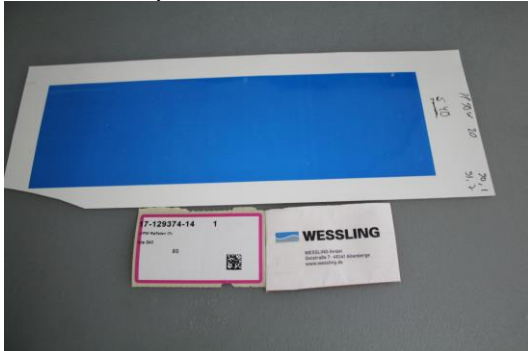
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Sample No. 17-129374-13



Sample No. 17-129374-14



Sample No. 17-129374-17



Sample No. 17-129374-18



Sample No. 17-129374-23



Sample No. 17-129374-25



Sample No. 17-129374-27



Sample No. 17-129374-28



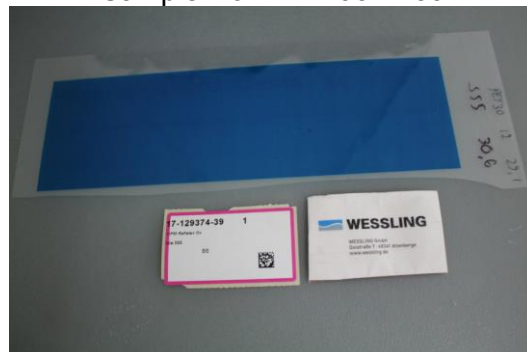
Sample No. 17-129374-35



Sample No. 17-129374-37



Sample No. 17-129374-39



Sample No. 17-129374-41



Sample No. 17-129374-44



Analysed samples/parts:

Sample No.	Sample identifier
17-122906-04	Sample complete (food contact side)
17-122906-05	Sample complete (food contact side)
17-122906-09	Sample complete (food contact side)
17-122906-12	Sample complete (food contact side)
17-129374-02	Sample complete (food contact side)
17-129374-07	Sample complete (food contact side)
17-129374-08	Sample complete (food contact side)
17-129374-13	Sample complete (food contact side)
17-129374-14	Sample complete (food contact side)
17-129374-17	Sample complete (food contact side)
17-129374-18	Sample complete (food contact side)
17-129374-23	Sample complete (food contact side)
17-129374-25	Sample complete (food contact side)
17-129374-27	Sample complete (food contact side)
17-129374-28	Sample complete (food contact side)
17-129374-35	Sample complete (food contact side)
17-129374-37	Sample complete (food contact side)
17-129374-39	Sample complete (food contact side)
17-129374-41	Sample complete (food contact side)
17-129374-44	Sample complete (food contact side)

Examination methods:

Parameter	Method	Performing place
Preparation specific migration	DIN EN 13130-1 mod.	Produktanalytik Altenberge
Acrylates	WEX 1061	*

* tested by a cooperation laboratory

Results:

1. Acrylates

Test conditions:

Ethanol 95% (v/v)

10 d, 40 °C

S:V = 0,44 dm² : 75 ml

Parameter	CAS No.	Unit	17-122906-04 S4 Polyamide
2-Ethylhexyl acrylate	103-11-7	mg/kg	< 0,01
Benzyl methacrylate	2495-37-6	mg/kg	< 0,01
Butyl acrylate	141-32-2	mg/kg	< 0,1
Butyl methacrylate	97-88-1	mg/kg	< 0,1
Methyl methacrylate	80-62-6	mg/kg	< 0,1
Methyl acrylate	96-33-3	mg/kg	< 0,1
Ethyl acrylate	140-88-5	mg/kg	< 0,1
Ethylen dimethacrylate	97-90-5	mg/kg	< 0,01
Hexamethylene diacrylate	13048-33-4	mg/kg	< 0,01

Parameter	CAS No.	Unit	17-122906-05 S5 Polyamide
2-Ethylhexyl acrylate	103-11-7	mg/kg	< 0,01
Benzyl methacrylate	2495-37-6	mg/kg	< 0,01
Butyl acrylate	141-32-2	mg/kg	< 0,1
Butyl methacrylate	97-88-1	mg/kg	< 0,1
Methyl methacrylate	80-62-6	mg/kg	< 0,1
Methyl acrylate	96-33-3	mg/kg	< 0,1
Ethyl acrylate	140-88-5	mg/kg	< 0,1
Ethylen dimethacrylate	97-90-5	mg/kg	< 0,01
Hexamethylene diacrylate	13048-33-4	mg/kg	< 0,01

Parameter	CAS No.	Unit	17-122906-09 S9 clear PP
2-Ethylhexyl acrylate	103-11-7	mg/kg	< 0,01
Benzyl methacrylate	2495-37-6	mg/kg	< 0,01
Butyl acrylate	141-32-2	mg/kg	< 0,1
Butyl methacrylate	97-88-1	mg/kg	< 0,1
Methyl methacrylate	80-62-6	mg/kg	< 0,1
Methyl acrylate	96-33-3	mg/kg	< 0,1
Ethyl acrylate	140-88-5	mg/kg	< 0,1
Ethylen dimethacrylate	97-90-5	mg/kg	< 0,01
Hexamethylene diacrylate	13048-33-4	mg/kg	< 0,01

Parameter	CAS No.	Unit	17-122906-12 S12 clear PP
2-Ethylhexyl acrylate	103-11-7	mg/kg	< 0,01
Benzyl methacrylate	2495-37-6	mg/kg	< 0,01
Butyl acrylate	141-32-2	mg/kg	< 0,1
Butyl methacrylate	97-88-1	mg/kg	< 0,1
Methyl methacrylate	80-62-6	mg/kg	< 0,1
Methyl acrylate	96-33-3	mg/kg	< 0,1
Ethyl acrylate	140-88-5	mg/kg	< 0,1
Ethylen dimethacrylate	97-90-5	mg/kg	< 0,01
Hexamethylene diacrylate	13048-33-4	mg/kg	< 0,01

Parameter	CAS No.	Unit	17-129374-02 S19 very thin PP
2-Ethylhexyl acrylate	103-11-7	mg/kg	< 0,01
Benzyl methacrylate	2495-37-6	mg/kg	< 0,01
Butyl acrylate	141-32-2	mg/kg	< 0,1
Butyl methacrylate	97-88-1	mg/kg	< 0,1
Methyl methacrylate	80-62-6	mg/kg	< 0,1
Methyl acrylate	96-33-3	mg/kg	< 0,1
Ethyl acrylate	140-88-5	mg/kg	< 0,1
Ethylen dimethacrylate	97-90-5	mg/kg	< 0,01
Hexamethylene diacrylate	13048-33-4	mg/kg	< 0,01

Parameter	CAS No.	Unit	17-129374-07 S25 clear PE
2-Ethylhexyl acrylate	103-11-7	mg/kg	< 0,01
Benzyl methacrylate	2495-37-6	mg/kg	< 0,01
Butyl acrylate	141-32-2	mg/kg	< 0,1
Butyl methacrylate	97-88-1	mg/kg	< 0,1
Methyl methacrylate	80-62-6	mg/kg	< 0,1
Methyl acrylate	96-33-3	mg/kg	< 0,1
Ethyl acrylate	140-88-5	mg/kg	< 0,1
Ethylen dimethacrylate	97-90-5	mg/kg	< 0,01
Hexamethylene diacrylate	13048-33-4	mg/kg	< 0,01

Parameter	CAS No.	Unit	17-129374-08 S26 clear PE
2-Ethylhexyl acrylate	103-11-7	mg/kg	< 0,01
Benzyl methacrylate	2495-37-6	mg/kg	< 0,01
Butyl acrylate	141-32-2	mg/kg	< 0,1
Butyl methacrylate	97-88-1	mg/kg	< 0,1
Methyl methacrylate	80-62-6	mg/kg	< 0,1
Methyl acrylate	96-33-3	mg/kg	< 0,1
Ethyl acrylate	140-88-5	mg/kg	< 0,1
Ethylen dimethacrylate	97-90-5	mg/kg	< 0,01
Hexamethylene diacrylate	13048-33-4	mg/kg	< 0,01

Parameter	CAS No.	Unit	17-129374-13 S39 thick white PE
2-Ethylhexyl acrylate	103-11-7	mg/kg	< 0,01
Benzyl methacrylate	2495-37-6	mg/kg	< 0,01
Butyl acrylate	141-32-2	mg/kg	< 0,1
Butyl methacrylate	97-88-1	mg/kg	< 0,1
Methyl methacrylate	80-62-6	mg/kg	< 0,1
Methyl acrylate	96-33-3	mg/kg	< 0,1
Ethyl acrylate	140-88-5	mg/kg	< 0,1
Ethylen dimethacrylate	97-90-5	mg/kg	< 0,01
Hexamethylene diacrylate	13048-33-4	mg/kg	< 0,01

Parameter	CAS No.	Unit	17-129374-14 S40 thick white PE
2-Ethylhexyl acrylate	103-11-7	mg/kg	< 0,01
Benzyl methacrylate	2495-37-6	mg/kg	< 0,01
Butyl acrylate	141-32-2	mg/kg	< 0,1
Butyl methacrylate	97-88-1	mg/kg	< 0,1
Methyl methacrylate	80-62-6	mg/kg	< 0,1
Methyl acrylate	96-33-3	mg/kg	< 0,1
Ethyl acrylate	140-88-5	mg/kg	< 0,1
Ethylen dimethacrylate	97-90-5	mg/kg	< 0,01
Hexamethylene diacrylate	13048-33-4	mg/kg	< 0,01

Parameter	CAS No.	Unit	17-129374-17 S43 white PP
2-Ethylhexyl acrylate	103-11-7	mg/kg	< 0,01
Benzyl methacrylate	2495-37-6	mg/kg	< 0,01
Butyl acrylate	141-32-2	mg/kg	< 0,1
Butyl methacrylate	97-88-1	mg/kg	< 0,1
Methyl methacrylate	80-62-6	mg/kg	< 0,1
Methyl acrylate	96-33-3	mg/kg	< 0,1
Ethyl acrylate	140-88-5	mg/kg	< 0,1
Ethylen dimethacrylate	97-90-5	mg/kg	< 0,01
Hexamethylene diacrylate	13048-33-4	mg/kg	< 0,01

Parameter	CAS No.	Unit	17-129374-18 S44 white PP
2-Ethylhexyl acrylate	103-11-7	mg/kg	< 0,01
Benzyl methacrylate	2495-37-6	mg/kg	< 0,01
Butyl acrylate	141-32-2	mg/kg	< 0,1
Butyl methacrylate	97-88-1	mg/kg	< 0,1
Methyl methacrylate	80-62-6	mg/kg	< 0,1
Methyl acrylate	96-33-3	mg/kg	< 0,1
Ethyl acrylate	140-88-5	mg/kg	< 0,1
Ethylen dimethacrylate	97-90-5	mg/kg	< 0,01
Hexamethylene diacrylate	13048-33-4	mg/kg	< 0,01

Parameter	CAS No.	Unit	17-129374-23 S49 thin PET
2-Ethylhexyl acrylate	103-11-7	mg/kg	< 0,01
Benzyl methacrylate	2495-37-6	mg/kg	< 0,01
Butyl acrylate	141-32-2	mg/kg	< 0,1
Butyl methacrylate	97-88-1	mg/kg	< 0,1
Methyl methacrylate	80-62-6	mg/kg	< 0,1
Methyl acrylate	96-33-3	mg/kg	< 0,1
Ethyl acrylate	140-88-5	mg/kg	< 0,1
Ethylen dimethacrylate	97-90-5	mg/kg	< 0,01
Hexamethylene diacrylate	13048-33-4	mg/kg	< 0,01

Parameter	CAS No.	Unit	17-129374-25 S51 thin PET
2-Ethylhexyl acrylate	103-11-7	mg/kg	< 0,01
Benzyl methacrylate	2495-37-6	mg/kg	< 0,01
Butyl acrylate	141-32-2	mg/kg	< 0,1
Butyl methacrylate	97-88-1	mg/kg	< 0,1
Methyl methacrylate	80-62-6	mg/kg	< 0,1
Methyl acrylate	96-33-3	mg/kg	< 0,1
Ethyl acrylate	140-88-5	mg/kg	< 0,1
Ethylen dimethacrylate	97-90-5	mg/kg	< 0,01
Hexamethylene diacrylate	13048-33-4	mg/kg	< 0,01

Parameter	CAS No.	Unit	17-129374-27 S31 white PE
2-Ethylhexyl acrylate	103-11-7	mg/kg	< 0,01
Benzyl methacrylate	2495-37-6	mg/kg	< 0,01
Butyl acrylate	141-32-2	mg/kg	< 0,1
Butyl methacrylate	97-88-1	mg/kg	< 0,1
Methyl methacrylate	80-62-6	mg/kg	< 0,1
Methyl acrylate	96-33-3	mg/kg	< 0,1
Ethyl acrylate	140-88-5	mg/kg	< 0,1
Ethylen dimethacrylate	97-90-5	mg/kg	< 0,01
Hexamethylene diacrylate	13048-33-4	mg/kg	< 0,01

Parameter	CAS No.	Unit	17-129374-28 S32 white PE
2-Ethylhexyl acrylate	103-11-7	mg/kg	< 0,01
Benzyl methacrylate	2495-37-6	mg/kg	< 0,01
Butyl acrylate	141-32-2	mg/kg	< 0,1
Butyl methacrylate	97-88-1	mg/kg	< 0,1
Methyl methacrylate	80-62-6	mg/kg	< 0,1
Methyl acrylate	96-33-3	mg/kg	< 0,1
Ethyl acrylate	140-88-5	mg/kg	< 0,1
Ethylen dimethacrylate	97-90-5	mg/kg	< 0,01
Hexamethylene diacrylate	13048-33-4	mg/kg	< 0,01

Parameter	CAS No.	Unit	17-129374-35 S17 very thin PP
2-Ethylhexyl acrylate	103-11-7	mg/kg	< 0,01
Benzyl methacrylate	2495-37-6	mg/kg	< 0,01
Butyl acrylate	141-32-2	mg/kg	< 0,1
Butyl methacrylate	97-88-1	mg/kg	< 0,1
Methyl methacrylate	80-62-6	mg/kg	< 0,1
Methyl acrylate	96-33-3	mg/kg	< 0,1
Ethyl acrylate	140-88-5	mg/kg	< 0,1
Ethylen dimethacrylate	97-90-5	mg/kg	< 0,01
Hexamethylene diacrylate	13048-33-4	mg/kg	< 0,01

Parameter	CAS No.	Unit	17-129374-37 S53 PET
2-Ethylhexyl acrylate	103-11-7	mg/kg	< 0,01
Benzyl methacrylate	2495-37-6	mg/kg	< 0,01
Butyl acrylate	141-32-2	mg/kg	< 0,1
Butyl methacrylate	97-88-1	mg/kg	< 0,1
Methyl methacrylate	80-62-6	mg/kg	< 0,1
Methyl acrylate	96-33-3	mg/kg	< 0,1
Ethyl acrylate	140-88-5	mg/kg	< 0,1
Ethylen dimethacrylate	97-90-5	mg/kg	< 0,01
Hexamethylene diacrylate	13048-33-4	mg/kg	< 0,01

Parameter	CAS No.	Unit	17-129374-39 S55 PET
2-Ethylhexyl acrylate	103-11-7	mg/kg	< 0,01
Benzyl methacrylate	2495-37-6	mg/kg	< 0,01
Butyl acrylate	141-32-2	mg/kg	< 0,1
Butyl methacrylate	97-88-1	mg/kg	< 0,1
Methyl methacrylate	80-62-6	mg/kg	< 0,1
Methyl acrylate	96-33-3	mg/kg	< 0,1
Ethyl acrylate	140-88-5	mg/kg	< 0,1
Ethylen dimethacrylate	97-90-5	mg/kg	< 0,01
Hexamethylene diacrylate	13048-33-4	mg/kg	< 0,01

Parameter	CAS No.	Unit	17-129374-41 S57 white thick PE
2-Ethylhexyl acrylate	103-11-7	mg/kg	< 0,01
Benzyl methacrylate	2495-37-6	mg/kg	< 0,01
Butyl acrylate	141-32-2	mg/kg	< 0,1
Butyl methacrylate	97-88-1	mg/kg	< 0,1
Methyl methacrylate	80-62-6	mg/kg	< 0,1
Methyl acrylate	96-33-3	mg/kg	< 0,1
Ethyl acrylate	140-88-5	mg/kg	< 0,1
Ethylen dimethacrylate	97-90-5	mg/kg	< 0,01
Hexamethylene diacrylate	13048-33-4	mg/kg	< 0,01

Parameter	CAS No.	Unit	17-129374-44 S60 white thick PE
2-Ethylhexyl acrylate	103-11-7	mg/kg	< 0,01
Benzyl methacrylate	2495-37-6	mg/kg	< 0,01
Butyl acrylate	141-32-2	mg/kg	< 0,1
Butyl methacrylate	97-88-1	mg/kg	< 0,1
Methyl methacrylate	80-62-6	mg/kg	< 0,1
Methyl acrylate	96-33-3	mg/kg	< 0,1
Ethyl acrylate	140-88-5	mg/kg	< 0,1
Ethylen dimethacrylate	97-90-5	mg/kg	< 0,01
Hexamethylene diacrylate	13048-33-4	mg/kg	< 0,01

Johannes Wächter
 (Food Chemist / Scientific Expert)

Report No. CAL17-129906-1/hve

Altenberge, 24th October 2017**Material testing**

- Sample receipt: 17th August 2017
- Client: UPM Raflatac Oy, Tesomankatu 31,
33101 Tampere, Finland
- Order date: In written form dated 29th August 2017
- Sampled by: Client
- Beginning of examinations: 13th September 2017
- End of examinations: 24th October 2017
- Sample No. 17-122906-01: S1 (polyamide)
Sample No. 17-122906-03: S3 (polyamide)
Sample No. 17-122906-15: S15 (clear PP)
Sample No. 17-122906-16: S16 (clear PP)
Sample No. 17-129374-01: S18 (very thin PET)
Sample No. 17-129374-03: S21 (very thin PET)
Sample No. 17-129374-09: S27 (clear PE)
Sample No. 17-129374-10: S28 (clear PE)
Sample No. 17-129374-11: S29 (white PE)
Sample No. 17-129374-12: S38 (thick white PP)
Sample No. 17-129374-15: S41 (white PP)
Sample No. 17-129374-20: S46 (white PP)
Sample No. 17-129374-21: S47 (thin PET)
Sample No. 17-129374-26: S52 (thin PET)
Sample No. 17-129374-32: S37 (thick white PP)
Sample No. 17-129374-34: S30 (white PE)
Sample No. 17-129374-38: S54 (PET)
Sample No. 17-129374-40: S56 (PET)
Sample No. 17-129374-42: S58 (white thick PE)
Sample No. 17-129374-46: S62 (white thick PE)
- Further information: -/-

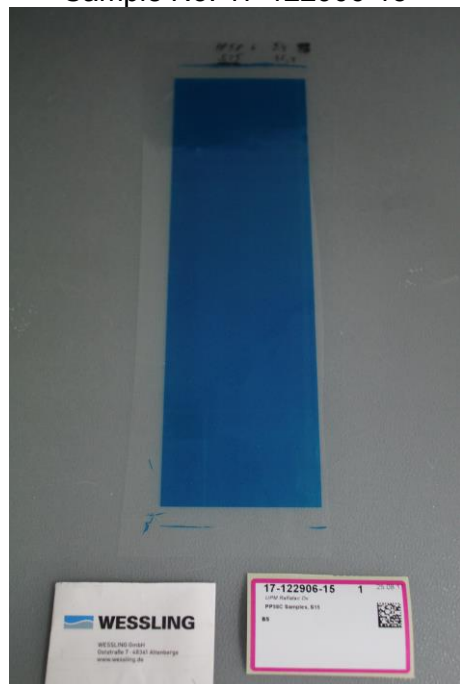
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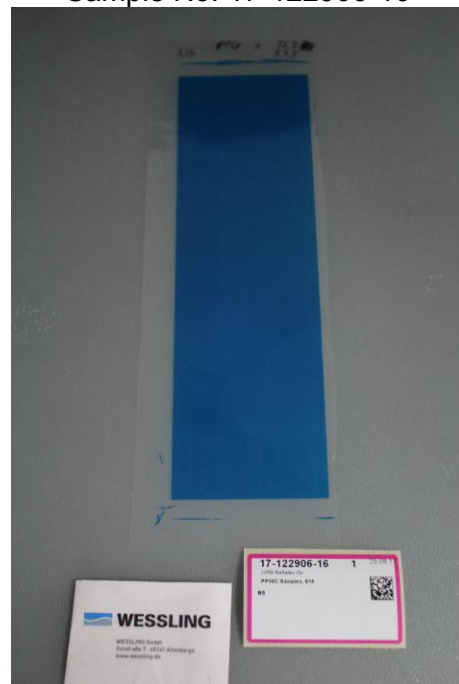
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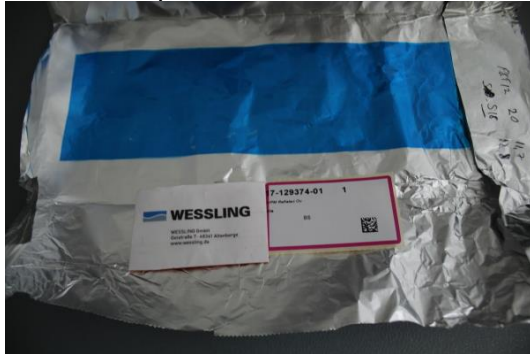
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Sample No. 17-122906-16



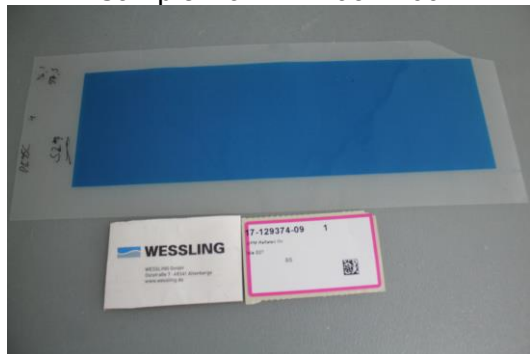
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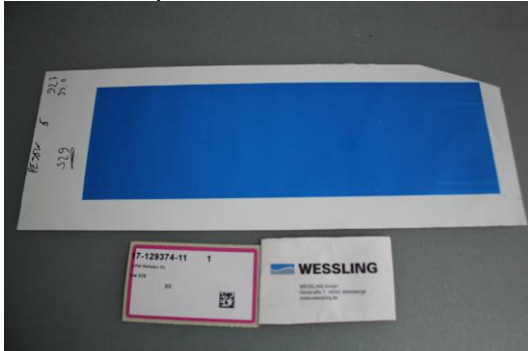
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Sample No. 17-129374-10



Sample No. 17-129374-11



Sample No. 17-129374-12



Sample No. 17-129374-15



Sample No. 17-129374-20



Sample No. 17-129374-21



Sample No. 17-129374-26



Sample No. 17-129374-32



Sample No. 17-129374-34



Sample No. 17-129374-38



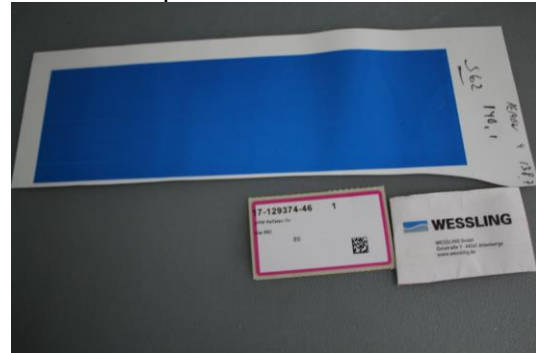
Sample No. 17-129374-40



Sample No. 17-129374-42



Sample No. 17-129374-46



Analysed samples/parts:

Sample No.	Sample identifier
17-122906-01	Sample complete (food contact side)
17-122906-03	Sample complete (food contact side)
17-122906-15	Sample complete (food contact side)
17-122906-16	Sample complete (food contact side)
17-129374-01	Sample complete (food contact side)
17-129374-03	Sample complete (food contact side)
17-129374-09	Sample complete (food contact side)
17-129374-10	Sample complete (food contact side)
17-129374-11	Sample complete (food contact side)
17-129374-12	Sample complete (food contact side)
17-129374-15	Sample complete (food contact side)
17-129374-20	Sample complete (food contact side)
17-129374-21	Sample complete (food contact side)
17-129374-26	Sample complete (food contact side)
17-129374-32	Sample complete (food contact side)
17-129374-34	Sample complete (food contact side)
17-129374-38	Sample complete (food contact side)
17-129374-40	Sample complete (food contact side)
17-129374-42	Sample complete (food contact side)
17-129374-46	Sample complete (food contact side)

Examination methods:

Parameter	Method	Performing place
Preparation specific migration	DIN EN 13130-1 mod.	Produktanalytik Altenberge
Primary aromatic amines	ASU L 00.00-6 ^A	Produktanalytik Altenberge
Primary aromatic amines (single substances)	WBSE-98, (LC-MS/MS)	* Produktanalytik Budapest

* not within the national accreditation of WESSLING GmbH

Results:

1. Primary aromatic amines

1.1 Primary aromatic amines, calculated as aniline hydrochloride

Test conditions:

Acetic acid 3% (w/w)

10 d, 40 °C

O:V = 0,88 dm² : 150 ml

Food simulant	Unit	17-122906-01 S1 (polyamide)
Acetic acid 3%	mg/kg	0,05

Food simulant	Unit	17-122906-03 S3 (polyamide)
Acetic acid 3%	mg/kg	0,05

Food simulant	Unit	17-122906-15 S15 (clear PP)
Acetic acid 3%	mg/kg	< 0,01

Food simulant	Unit	17-122906-16 S16 (clear PP)
Acetic acid 3%	mg/kg	0,02

Food simulant	Unit	17-129374-01 S18 (very thin PET)
Acetic acid 3%	mg/kg	< 0,01

Food simulant	Unit	17-129374-03 S21 (very thin PET)
Acetic acid 3%	mg/kg	< 0,01

Food simulant	Unit	17-129374-09 S27 (clear PE)
Acetic acid 3%	mg/kg	0,03

Food simulant	Unit	17-129374-10 S28 (clear PE)
Acetic acid 3%	mg/kg	0,03

Food simulant	Unit	17-129374-11 S29 (white PE)
Acetic acid 3%	mg/kg	0,03

Food simulant	Unit	17-129374-12 S38 (thick white PP)
Acetic acid 3%	mg/kg	< 0,01

Food simulant	Unit	17-129374-15 S41 (white PP)
Acetic acid 3%	mg/kg	< 0,01

Food simulant	Unit	17-129374-20 S46 (white PP)
Acetic acid 3%	mg/kg	< 0,01

Food simulant	Unit	17-129374-21 S47 (thin PET)
Acetic acid 3%	mg/kg	< 0,01

Food simulant	Unit	17-129374-26 S52 (thin PET)
Acetic acid 3%	mg/kg	< 0,01

Food simulant	Unit	17-129374-32 S37 (thick white PP)
Acetic acid 3%	mg/kg	< 0,01

Food simulant	Unit	17-129374-34 S30 (white PE)
Acetic acid 3%	mg/kg	0,03

Food simulant	Unit	17-129374-38 S54 (PET)
Acetic acid 3%	mg/kg	< 0,01

Food simulant	Unit	17-129374-40 S56 (PET)
Acetic acid 3%	mg/kg	< 0,01

Food simulant	Unit	17-129374-42 S58 (white thick PE)
Acetic acid 3%	mg/kg	0,02

Food simulant	Unit	17-129374-46 S62 (white thick PE)
Acetic acid 3%	mg/kg	0,02

1.2 Primary aromatic amines (single substances)

Test conditions:

Acetic acid 3%

2 h, 70 °C

O:V = 1,8 dm² : 200 ml

Parameter	Unit	17-122906-01 S1 (polyamide)
2,4,5-Trimethylaniline	µg/kg	<0,1
p-Cresidine	µg/kg	<0,1
2,4-Toluylendiamine	µg/kg	<0,1
2-Methyl-5-nitroaniline	µg/kg	<0,25
2-Naphthylamine	µg/kg	<0,1
3,3'-Dichlorobenzidine	µg/kg	<0,1
3,3'-Dimethoxybenzidine	µg/kg	<0,1
3,3'-Dimethyl-4,4'-diaminodiphenylmethane	µg/kg	<0,1
3,3'-Dimethylbenzidine	µg/kg	<0,1
4,4'-Diaminodiphenylmethane	µg/kg	<0,1
4,4'-methylen-bis-(2-chloroaniline)	µg/kg	<0,1
4,4'-Oxydianiline	µg/kg	<0,1
4,4'-Thiodianiline	µg/kg	<0,1
4-Aminoazobenzene	µg/kg	<0,1
4-Aminodiphenyle	µg/kg	<0,1
4-Chloroaniline	µg/kg	<0,1
Aniline	µg/kg	<0,1
Benzidine	µg/kg	<0,1
o-Aminoazotoluene	µg/kg	<0,1
4-Chloro-o-toluidine	µg/kg	<0,1
o-Anisidine	µg/kg	<0,1
o-Toluidine	µg/kg	<0,1

UPM Raflatac Oy/CAL 17-129906-1/hve

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Geschäftsführer:
Julia Weßling, Florian Weßling
AG Steinfurt HRB 1953

Parameter	Unit	17-122906-01 S1 (polyamide)
2,4 Diaminoanisole	µg/kg	<0,1
p-Toluidine	µg/kg	<0,1

Parameter	Unit	17-122906-03 S3 (polyamide)
2,4,5-Trimethylaniline	µg/kg	<0,1
p-Cresidine	µg/kg	<0,1
2,4-Toluylendiamine	µg/kg	<0,1
2-Methyl-5-nitroaniline	µg/kg	<0,25
2-Naphthylamine	µg/kg	<0,1
3,3'-Dichlorobenzidine	µg/kg	<0,1
3,3'-Dimethoxybenzidine	µg/kg	<0,1
3,3'-Dimethyl-4,4'-diaminodiphenylmethane	µg/kg	<0,1
3,3'-Dimethylbenzidine	µg/kg	<0,1
4,4'-Diaminodiphenylmethane	µg/kg	<0,1
4,4'-methylen-bis-(2-chloroaniline)	µg/kg	<0,1
4,4'-Oxydianiline	µg/kg	<0,1
4,4'-Thiodianiline	µg/kg	<0,1
4-Aminoazobenzene	µg/kg	<0,1
4-Aminodiphenyle	µg/kg	<0,1
4-Chloroaniline	µg/kg	<0,1
Aniline	µg/kg	<0,1
Benzidine	µg/kg	<0,1
o-Aminoazotoluene	µg/kg	<0,1
4-Chloro-o-toluidine	µg/kg	<0,1
o-Anisidine	µg/kg	<0,1
o-Toluidine	µg/kg	<0,1

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Geschäftsführer:
Julia Weßling, Florian Weßling
AG Steinfurt HRB 1953

Parameter	Unit	17-122906-03 S3 (polyamide)
2,4 Diaminoanisole	µg/kg	<0,1
p-Toluidine	µg/kg	<0,1

Parameter	Unit	17-122906-15 S15 (clear PP)
2,4,5-Trimethylaniline	µg/kg	<0,1
p-Cresidine	µg/kg	<0,1
2,4-Toluylendiamine	µg/kg	<0,1
2-Methyl-5-nitroaniline	µg/kg	<0,25
2-Naphthylamine	µg/kg	<0,1
3,3'-Dichlorobenzidine	µg/kg	<0,1
3,3'-Dimethoxybenzidine	µg/kg	<0,1
3,3'-Dimethyl-4,4'-diaminodiphenylmethane	µg/kg	<0,1
3,3'-Dimethylbenzidine	µg/kg	<0,1
4,4'-Diaminodiphenylmethane	µg/kg	<0,1
4,4'-methylen-bis-(2-chloroaniline)	µg/kg	<0,1
4,4'-Oxydianiline	µg/kg	<0,1
4,4'-Thiodianiline	µg/kg	<0,1
4-Aminoazobenzene	µg/kg	<0,1
4-Aminodiphenyle	µg/kg	<0,1
4-Chloroaniline	µg/kg	<0,1
Aniline	µg/kg	<0,1
Benzidine	µg/kg	<0,1
o-Aminoazotoluene	µg/kg	<0,1
4-Chloro-o-toluidine	µg/kg	<0,1
o-Anisidine	µg/kg	<0,1
o-Toluidine	µg/kg	<0,1

Parameter	Unit	17-122906-15 S15 (clear PP)
2,4 Diaminoanisole	µg/kg	<0,1
p-Toluidine	µg/kg	<0,1

Parameter	Unit	17-122906-16 S16 (clear PP)
2,4,5-Trimethylaniline	µg/kg	<0,1
p-Cresidine	µg/kg	<0,1
2,4-Toluylendiamine	µg/kg	<0,1
2-Methyl-5-nitroaniline	µg/kg	<0,25
2-Naphthylamine	µg/kg	<0,1
3,3'-Dichlorobenzidine	µg/kg	<0,1
3,3'-Dimethoxybenzidine	µg/kg	<0,1
3,3'-Dimethyl-4,4'-diaminodiphenylmethane	µg/kg	<0,1
3,3'-Dimethylbenzidine	µg/kg	<0,1
4,4'-Diaminodiphenylmethane	µg/kg	<0,1
4,4'-methylen-bis-(2-chloroaniline)	µg/kg	<0,1
4,4'-Oxydianiline	µg/kg	<0,1
4,4'-Thiodianiline	µg/kg	<0,1
4-Aminoazobenzene	µg/kg	<0,1
4-Aminodiphenyle	µg/kg	<0,1
4-Chloroaniline	µg/kg	<0,1
Aniline	µg/kg	<0,1
Benzidine	µg/kg	<0,1
o-Aminoazotoluene	µg/kg	<0,1
4-Chloro-o-toluidine	µg/kg	<0,1
o-Anisidine	µg/kg	<0,1

Parameter	Unit	17-122906-16 S16 (clear PP)
o-Toluidine	µg/kg	<0,1
2,4 Diaminoanisole	µg/kg	<0,1
p-Toluidine	µg/kg	<0,1

Parameter	Unit	17-129374-01 S18 (very thin PET)
2,4,5-Trimethylaniline	µg/kg	<0,1
p-Cresidine	µg/kg	<0,1
2,4-Toluylendiamine	µg/kg	<0,1
2-Methyl-5-nitroaniline	µg/kg	<0,25
2-Naphthylamine	µg/kg	<0,1
3,3'-Dichlorobenzidine	µg/kg	<0,1
3,3'-Dimethoxybenzidine	µg/kg	<0,1
3,3'-Dimethyl-4,4'- diaminodiphenylmethane	µg/kg	<0,1
3,3'-Dimethylbenzidine	µg/kg	<0,1
4,4'-Diaminodiphenyl- methane	µg/kg	<0,1
4,4'-methylen-bis-(2- chloroaniline)	µg/kg	<0,1
4,4'-Oxydianiline	µg/kg	<0,1
4,4'-Thiodianiline	µg/kg	<0,1
4-Aminoazobenzene	µg/kg	<0,1
4-Aminodiphenyle	µg/kg	<0,1
4-Chloroaniline	µg/kg	<0,1
Aniline	µg/kg	<0,1
Benzidine	µg/kg	<0,1
o-Aminoazotoluene	µg/kg	<0,1
4-Chloro-o-toluidine	µg/kg	<0,1

Parameter	Unit	17-129374-01 S18 (very thin PET)
o-Anisidine	µg/kg	<0,1
o-Toluidine	µg/kg	<0,1
2,4 Diaminoanisole	µg/kg	<0,1
p-Toluidine	µg/kg	<0,1

Parameter	Unit	17-129374-03 S21 (very thin PET)
2,4,5-Trimethylaniline	µg/kg	<0,1
p-Cresidine	µg/kg	<0,1
2,4-Toluylendiamine	µg/kg	<0,1
2-Methyl-5-nitroaniline	µg/kg	<0,25
2-Naphthylamine	µg/kg	<0,1
3,3'-Dichlorobenzidine	µg/kg	<0,1
3,3'-Dimethoxybenzidine	µg/kg	<0,1
3,3'-Dimethyl-4,4'- diaminodiphenylmethane	µg/kg	<0,1
3,3'-Dimethylbenzidine	µg/kg	<0,1
4,4'-Diaminodiphenyl- methane	µg/kg	<0,1
4,4'-methylen-bis-(2- chloroaniline)	µg/kg	<0,1
4,4'-Oxydianiline	µg/kg	<0,1
4,4'-Thiodianiline	µg/kg	<0,1
4-Aminoazobenzene	µg/kg	<0,1
4-Aminodiphenyle	µg/kg	<0,1
4-Chloroaniline	µg/kg	<0,1
Aniline	µg/kg	<0,1
Benzidine	µg/kg	<0,1
o-Aminoazotoluene	µg/kg	<0,1

Parameter	Unit	17-129374-03 S21 (very thin PET)
4-Chloro-o-toluidine	µg/kg	<0,1
o-Anisidine	µg/kg	<0,1
o-Toluidine	µg/kg	<0,1
2,4 Diaminoanisole	µg/kg	<0,1
p-Toluidine	µg/kg	<0,1

Parameter	Unit	17-129374-09 S27 (clear PE)
2,4,5-Trimethylaniline	µg/kg	<0,1
p-Cresidine	µg/kg	<0,1
2,4-Toluylendiamine	µg/kg	<0,1
2-Methyl-5-nitroaniline	µg/kg	<0,25
2-Naphthylamine	µg/kg	<0,1
3,3'-Dichlorobenzidine	µg/kg	<0,1
3,3'-Dimethoxybenzidine	µg/kg	<0,1
3,3'-Dimethyl-4,4'-diaminodiphenylmethane	µg/kg	<0,1
3,3'-Dimethylbenzidine	µg/kg	<0,1
4,4'-Diaminodiphenylmethane	µg/kg	<0,1
4,4'-methylen-bis-(2-chloroaniline)	µg/kg	<0,1
4,4'-Oxydianiline	µg/kg	<0,1
4,4'-Thiodianiline	µg/kg	<0,1
4-Aminoazobenzene	µg/kg	<0,1
4-Aminodiphenyle	µg/kg	<0,1
4-Chloroaniline	µg/kg	<0,1
Aniline	µg/kg	<0,1
Benzidine	µg/kg	<0,1

Parameter	Unit	17-129374-09 S27 (clear PE)
o-Aminoazotoluene	µg/kg	<0,1
4-Chloro-o-toluidine	µg/kg	<0,1
o-Anisidine	µg/kg	<0,1
o-Toluidine	µg/kg	<0,1
2,4 Diaminoanisole	µg/kg	<0,1
p-Toluidine	µg/kg	<0,1

Parameter	Unit	17-129374-10 S28 (clear PE)
2,4,5-Trimethylaniline	µg/kg	<0,1
p-Cresidine	µg/kg	<0,1
2,4-Toluylendiamine	µg/kg	<0,1
2-Methyl-5-nitroaniline	µg/kg	<0,25
2-Naphthylamine	µg/kg	<0,1
3,3'-Dichlorobenzidine	µg/kg	<0,1
3,3'-Dimethoxybenzidine	µg/kg	<0,1
3,3'-Dimethyl-4,4'-diaminodiphenylmethane	µg/kg	<0,1
3,3'-Dimethylbenzidine	µg/kg	<0,1
4,4'-Diaminodiphenylmethane	µg/kg	<0,1
4,4'-methylen-bis-(2-chloroaniline)	µg/kg	<0,1
4,4'-Oxydianiline	µg/kg	<0,1
4,4'-Thiodianiline	µg/kg	<0,1
4-Aminoazobenzene	µg/kg	<0,1
4-Aminodiphenyle	µg/kg	<0,1
4-Chloroaniline	µg/kg	<0,1
Aniline	µg/kg	<0,1
Benzidine	µg/kg	<0,1

Parameter	Unit	17-129374-10 S28 (clear PE)
o-Aminoazotoluene	µg/kg	<0,1
4-Chloro-o-toluidine	µg/kg	<0,1
o-Anisidine	µg/kg	<0,1
o-Toluidine	µg/kg	<0,1
2,4 Diaminoanisole	µg/kg	<0,1
p-Toluidine	µg/kg	<0,1

Parameter	Unit	17-129374-11 S29 (white PE)
2,4,5-Trimethylaniline	µg/kg	<0,1
p-Cresidine	µg/kg	<0,1
2,4-Toluylendiamine	µg/kg	<0,1
2-Methyl-5-nitroaniline	µg/kg	<0,25
2-Naphthylamine	µg/kg	<0,1
3,3'-Dichlorobenzidine	µg/kg	<0,1
3,3'-Dimethoxybenzidine	µg/kg	<0,1
3,3'-Dimethyl-4,4'-diaminodiphenylmethane	µg/kg	<0,1
3,3'-Dimethylbenzidine	µg/kg	<0,1
4,4'-Diaminodiphenylmethane	µg/kg	<0,1
4,4'-methylen-bis-(2-chloroaniline)	µg/kg	<0,1
4,4'-Oxydianiline	µg/kg	<0,1
4,4'-Thiodianiline	µg/kg	<0,1
4-Aminoazobenzene	µg/kg	<0,1
4-Aminodiphenyle	µg/kg	<0,1
4-Chloroaniline	µg/kg	<0,1
Aniline	µg/kg	<0,1

Parameter	Unit	17-129374-11 S29 (white PE)
Benzidine	µg/kg	<0,1
o-Aminoazotoluene	µg/kg	<0,1
4-Chloro-o-toluidine	µg/kg	<0,1
o-Anisidine	µg/kg	<0,1
o-Toluidine	µg/kg	<0,1
2,4 Diaminoanisole	µg/kg	<0,1
p-Toluidine	µg/kg	<0,1

Parameter	Unit	17-129374-12 S38 (thick white PP)
2,4,5-Trimethylaniline	µg/kg	<0,1
p-Cresidine	µg/kg	<0,1
2,4-Toluylendiamine	µg/kg	<0,1
2-Methyl-5-nitroaniline	µg/kg	<0,25
2-Naphthylamine	µg/kg	<0,1
3,3'-Dichlorobenzidine	µg/kg	<0,1
3,3'-Dimethoxybenzidine	µg/kg	<0,1
3,3'-Dimethyl-4,4'-diaminodiphenylmethane	µg/kg	<0,1
3,3'-Dimethylbenzidine	µg/kg	<0,1
4,4'-Diaminodiphenylmethane	µg/kg	<0,1
4,4'-methylen-bis-(2-chloroaniline)	µg/kg	<0,1
4,4'-Oxydianiline	µg/kg	<0,1
4,4'-Thiodianiline	µg/kg	<0,1
4-Aminoazobenzene	µg/kg	<0,1
4-Aminodiphenyle	µg/kg	<0,1
4-Chloroaniline	µg/kg	<0,1
Aniline	µg/kg	<0,1

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Geschäftsführer:
Julia Weßling, Florian Weßling
AG Steinfurt HRB 1953

Parameter	Unit	17-129374-12 S38 (thick white PP)
Benzidine	µg/kg	<0,1
o-Aminoazotoluene	µg/kg	<0,1
4-Chloro-o-toluidine	µg/kg	<0,1
o-Anisidine	µg/kg	<0,1
o-Toluidine	µg/kg	<0,1
2,4 Diaminoanisole	µg/kg	<0,1
p-Toluidine	µg/kg	<0,1

Parameter	Unit	17-129374-15 S41 (white PP)
2,4,5-Trimethylaniline	µg/kg	<0,1
p-Cresidine	µg/kg	<0,1
2,4-Toluylendiamine	µg/kg	<0,1
2-Methyl-5-nitroaniline	µg/kg	<0,25
2-Naphthylamine	µg/kg	<0,1
3,3'-Dichlorobenzidine	µg/kg	<0,1
3,3'-Dimethoxybenzidine	µg/kg	<0,1
3,3'-Dimethyl-4,4'-diaminodiphenylmethane	µg/kg	<0,1
3,3'-Dimethylbenzidine	µg/kg	<0,1
4,4'-Diaminodiphenylmethane	µg/kg	<0,1
4,4'-methylen-bis-(2-chloroaniline)	µg/kg	<0,1
4,4'-Oxydianiline	µg/kg	<0,1
4,4'-Thiodianiline	µg/kg	<0,1
4-Aminoazobenzene	µg/kg	<0,1
4-Aminodiphenyle	µg/kg	<0,1
4-Chloroaniline	µg/kg	<0,1

Parameter	Unit	17-129374-15 S41 (white PP)
Aniline	µg/kg	<0,1
Benzidine	µg/kg	<0,1
o-Aminoazotoluene	µg/kg	<0,1
4-Chloro-o-toluidine	µg/kg	<0,1
o-Anisidine	µg/kg	<0,1
o-Toluidine	µg/kg	<0,1
2,4 Diaminoanisole	µg/kg	<0,1
p-Toluidine	µg/kg	<0,1

Parameter	Unit	17-129374-20 S46 (white PP)
2,4,5-Trimethylaniline	µg/kg	<0,1
p-Cresidine	µg/kg	<0,1
2,4-Toluylendiamine	µg/kg	<0,1
2-Methyl-5-nitroaniline	µg/kg	<0,25
2-Naphthylamine	µg/kg	<0,1
3,3'-Dichlorobenzidine	µg/kg	<0,1
3,3'-Dimethoxybenzidine	µg/kg	<0,1
3,3'-Dimethyl-4,4'-diaminodiphenylmethane	µg/kg	<0,1
3,3'-Dimethylbenzidine	µg/kg	<0,1
4,4'-Diaminodiphenylmethane	µg/kg	<0,1
4,4'-methylen-bis-(2-chloroaniline)	µg/kg	<0,1
4,4'-Oxydianiline	µg/kg	<0,1
4,4'-Thiodianiline	µg/kg	<0,1
4-Aminoazobenzene	µg/kg	<0,1
4-Aminodiphenyle	µg/kg	<0,1

Parameter	Unit	17-129374-20 S46 (white PP)
4-Chloroaniline	µg/kg	<0,1
Aniline	µg/kg	<0,1
Benzidine	µg/kg	<0,1
o-Aminoazotoluene	µg/kg	<0,1
4-Chloro-o-toluidine	µg/kg	<0,1
o-Anisidine	µg/kg	<0,1
o-Toluidine	µg/kg	<0,1
2,4 Diaminoanisole	µg/kg	<0,1
p-Toluidine	µg/kg	<0,1

Parameter	Unit	17-129374-21 S47 (thin PET)
2,4,5-Trimethylaniline	µg/kg	<0,1
p-Cresidine	µg/kg	<0,1
2,4-Toluyldiamine	µg/kg	<0,1
2-Methyl-5-nitroaniline	µg/kg	<0,25
2-Naphthylamine	µg/kg	<0,1
3,3'-Dichlorobenzidine	µg/kg	<0,1
3,3'-Dimethoxybenzidine	µg/kg	<0,1
3,3'-Dimethyl-4,4'-diaminodiphenylmethane	µg/kg	<0,1
3,3'-Dimethylbenzidine	µg/kg	<0,1
4,4'-Diaminodiphenylmethane	µg/kg	<0,1
4,4'-methylen-bis-(2-chloroaniline)	µg/kg	<0,1
4,4'-Oxydianiline	µg/kg	<0,1
4,4'-Thiodianiline	µg/kg	<0,1
4-Aminoazobenzene	µg/kg	<0,1
4-Aminodiphenyle	µg/kg	<0,1

Parameter	Unit	17-129374-21 S47 (thin PET)
4-Chloroaniline	µg/kg	<0,1
Aniline	µg/kg	<0,1
Benzidine	µg/kg	<0,1
o-Aminoazotoluene	µg/kg	<0,1
4-Chloro-o-toluidine	µg/kg	<0,1
o-Anisidine	µg/kg	<0,1
o-Toluidine	µg/kg	<0,1
2,4 Diaminoanisole	µg/kg	<0,1
p-Toluidine	µg/kg	<0,1

Parameter	Unit	17-129374-26 S52 (thin PET)
2,4,5-Trimethylaniline	µg/kg	<0,1
p-Cresidine	µg/kg	<0,1
2,4-Toluyldiamine	µg/kg	<0,1
2-Methyl-5-nitroaniline	µg/kg	<0,25
2-Naphthylamine	µg/kg	<0,1
3,3'-Dichlorobenzidine	µg/kg	<0,1
3,3'-Dimethoxybenzidine	µg/kg	<0,1
3,3'-Dimethyl-4,4'-diaminodiphenylmethane	µg/kg	<0,1
3,3'-Dimethylbenzidine	µg/kg	<0,1
4,4'-Diaminodiphenylmethane	µg/kg	<0,1
4,4'-methylen-bis-(2-chloroaniline)	µg/kg	<0,1
4,4'-Oxydianiline	µg/kg	<0,1
4,4'-Thiodianiline	µg/kg	<0,1
4-Aminoazobenzene	µg/kg	<0,1
4-Aminodiphenyle	µg/kg	<0,1

Parameter	Unit	17-129374-26 S52 (thin PET)
4-Chloroaniline	µg/kg	<0,1
Aniline	µg/kg	<0,1
Benzidine	µg/kg	<0,1
o-Aminoazotoluene	µg/kg	<0,1
4-Chloro-o-toluidine	µg/kg	<0,1
o-Anisidine	µg/kg	<0,1
o-Toluidine	µg/kg	<0,1
2,4 Diaminoanisole	µg/kg	<0,1
p-Toluidine	µg/kg	<0,1

Parameter	Unit	17-129374-32 S37 (thick white PP)
2,4,5-Trimethylaniline	µg/kg	<0,1
p-Cresidine	µg/kg	<0,1
2,4-Toluylendiamine	µg/kg	<0,1
2-Methyl-5-nitroaniline	µg/kg	<0,25
2-Naphthylamine	µg/kg	<0,1
3,3'-Dichlorobenzidine	µg/kg	<0,1
3,3'-Dimethoxybenzidine	µg/kg	<0,1
3,3'-Dimethyl-4,4'- diaminodiphenylmethane	µg/kg	<0,1
3,3'-Dimethylbenzidine	µg/kg	<0,1
4,4'-Diaminodiphenyl- methane	µg/kg	<0,1
4,4'-methylen-bis-(2- chloroaniline)	µg/kg	<0,1
4,4'-Oxydianiline	µg/kg	<0,1
4,4'-Thiodianiline	µg/kg	<0,1
4-Aminoazobenzene	µg/kg	<0,1

Parameter	Unit	17-129374-32 S37 (thick white PP)
4-Aminodiphenyle	µg/kg	<0,1
4-Chloroaniline	µg/kg	<0,1
Aniline	µg/kg	<0,1
Benzidine	µg/kg	<0,1
o-Aminoazotoluene	µg/kg	<0,1
4-Chloro-o-toluidine	µg/kg	<0,1
o-Anisidine	µg/kg	<0,1
o-Toluidine	µg/kg	<0,1
2,4 Diaminoanisole	µg/kg	<0,1
p-Toluidine	µg/kg	<0,1

Parameter	Unit	17-129374-34 S30 (white PE)
2,4,5-Trimethylaniline	µg/kg	<0,1
p-Cresidine	µg/kg	<0,1
2,4-Toluyldiamine	µg/kg	<0,1
2-Methyl-5-nitroaniline	µg/kg	<0,25
2-Naphthylamine	µg/kg	<0,1
3,3'-Dichlorobenzidine	µg/kg	<0,1
3,3'-Dimethoxybenzidine	µg/kg	<0,1
3,3'-Dimethyl-4,4'- diaminodiphenylmethane	µg/kg	<0,1
3,3'-Dimethylbenzidine	µg/kg	<0,1
4,4'-Diaminodiphenyl- methane	µg/kg	<0,1
4,4'-methylen-bis-(2- chloroaniline)	µg/kg	<0,1
4,4'-Oxydianiline	µg/kg	<0,1
4,4'-Thiodianiline	µg/kg	<0,1
4-Aminoazobenzene	µg/kg	<0,1

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Geschäftsführer:
Julia Weßling, Florian Weßling
AG Steinfurt HRB 1953

Parameter	Unit	17-129374-34 S30 (white PE)
4-Aminodiphenyle	µg/kg	<0,1
4-Chloroaniline	µg/kg	<0,1
Aniline	µg/kg	<0,1
Benzidine	µg/kg	<0,1
o-Aminoazotoluene	µg/kg	<0,1
4-Chloro-o-toluidine	µg/kg	<0,1
o-Anisidine	µg/kg	<0,1
o-Toluidine	µg/kg	<0,1
2,4 Diaminoanisole	µg/kg	<0,1
p-Toluidine	µg/kg	<0,1

Parameter	Unit	17-129374-38 S54 (PET)
2,4,5-Trimethylaniline	µg/kg	<0,1
p-Cresidine	µg/kg	<0,1
2,4-Toluylendiamine	µg/kg	<0,1
2-Methyl-5-nitroaniline	µg/kg	<0,25
2-Naphthylamine	µg/kg	<0,1
3,3'-Dichlorobenzidine	µg/kg	<0,1
3,3'-Dimethoxybenzidine	µg/kg	<0,1
3,3'-Dimethyl-4,4'-diaminodiphenylmethane	µg/kg	<0,1
3,3'-Dimethylbenzidine	µg/kg	<0,1
4,4'-Diaminodiphenylmethane	µg/kg	<0,1
4,4'-methylen-bis-(2-chloroaniline)	µg/kg	<0,1
4,4'-Oxydianiline	µg/kg	<0,1
4,4'-Thiodianiline	µg/kg	<0,1
4-Aminoazobenzene	µg/kg	<0,1

Parameter	Unit	17-129374-38 S54 (PET)
4-Aminodiphenyle	µg/kg	<0,1
4-Chloroaniline	µg/kg	<0,1
Aniline	µg/kg	<0,1
Benzidine	µg/kg	<0,1
o-Aminoazotoluene	µg/kg	<0,1
4-Chloro-o-toluidine	µg/kg	<0,1
o-Anisidine	µg/kg	<0,1
o-Toluidine	µg/kg	<0,1
2,4 Diaminoanisole	µg/kg	<0,1
p-Toluidine	µg/kg	<0,1

Parameter	Unit	17-129374-40 S56 (PET)
2,4,5-Trimethylaniline	µg/kg	<0,1
p-Cresidine	µg/kg	<0,1
2,4-Toluylendiamine	µg/kg	<0,1
2-Methyl-5-nitroaniline	µg/kg	<0,25
2-Naphthylamine	µg/kg	<0,1
3,3'-Dichlorobenzidine	µg/kg	<0,1
3,3'-Dimethoxybenzidine	µg/kg	<0,1
3,3'-Dimethyl-4,4'-diaminodiphenylmethane	µg/kg	<0,1
3,3'-Dimethylbenzidine	µg/kg	<0,1
4,4'-Diaminodiphenylmethane	µg/kg	<0,1
4,4'-methylen-bis-(2-chloroaniline)	µg/kg	<0,1
4,4'-Oxydianiline	µg/kg	<0,1
4,4'-Thiodianiline	µg/kg	<0,1
4-Aminoazobenzene	µg/kg	<0,1

Parameter	Unit	17-129374-40 S56 (PET)
4-Aminodiphenyle	µg/kg	<0,1
4-Chloroaniline	µg/kg	<0,1
Aniline	µg/kg	<0,1
Benzidine	µg/kg	<0,1
o-Aminoazotoluene	µg/kg	<0,1
4-Chloro-o-toluidine	µg/kg	<0,1
o-Anisidine	µg/kg	<0,1
o-Toluidine	µg/kg	<0,1
2,4 Diaminoanisole	µg/kg	<0,1
p-Toluidine	µg/kg	<0,1

Parameter	Unit	17-129374-42 S58 (white thick PE)
2,4,5-Trimethylaniline	µg/kg	<0,1
p-Cresidine	µg/kg	<0,1
2,4-Toluylendiamine	µg/kg	<0,1
2-Methyl-5-nitroaniline	µg/kg	<0,25
2-Naphthylamine	µg/kg	<0,1
3,3'-Dichlorobenzidine	µg/kg	<0,1
3,3'-Dimethoxybenzidine	µg/kg	<0,1
3,3'-Dimethyl-4,4'-diaminodiphenylmethane	µg/kg	<0,1
3,3'-Dimethylbenzidine	µg/kg	<0,1
4,4'-Diaminodiphenylmethane	µg/kg	<0,1
4,4'-methylen-bis-(2-chloroaniline)	µg/kg	<0,1
4,4'-Oxydianiline	µg/kg	<0,1
4,4'-Thiodianiline	µg/kg	<0,1
4-Aminoazobenzene	µg/kg	<0,1

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Geschäftsführer:
Julia Weßling, Florian Weßling
AG Steinfurt HRB 1953

Parameter	Unit	17-129374-42 S58 (white thick PE)
4-Aminodiphenyle	µg/kg	<0,1
4-Chloroaniline	µg/kg	<0,1
Aniline	µg/kg	<0,1
Benzidine	µg/kg	<0,1
o-Aminoazotoluene	µg/kg	<0,1
4-Chloro-o-toluidine	µg/kg	<0,1
o-Anisidine	µg/kg	<0,1
o-Toluidine	µg/kg	<0,1
2,4 Diaminoanisole	µg/kg	<0,1
p-Toluidine	µg/kg	<0,1

Parameter	Unit	17-129374-46 S62 (white thick PE)
2,4,5-Trimethylaniline	µg/kg	<0,1
p-Cresidine	µg/kg	<0,1
2,4-Toluylendiamine	µg/kg	<0,1
2-Methyl-5-nitroaniline	µg/kg	<0,25
2-Naphthylamine	µg/kg	<0,1
3,3'-Dichlorobenzidine	µg/kg	<0,1
3,3'-Dimethoxybenzidine	µg/kg	<0,1
3,3'-Dimethyl-4,4'- diaminodiphenylmethane	µg/kg	<0,1
3,3'-Dimethylbenzidine	µg/kg	<0,1
4,4'-Diaminodiphenyl- methane	µg/kg	<0,1
4,4'-methylen-bis-(2- chloroaniline)	µg/kg	<0,1
4,4'-Oxydianiline	µg/kg	<0,1
4,4'-Thiodianiline	µg/kg	<0,1

Parameter	Unit	17-129374-46 S62 (white thick PE)
4-Aminoazobenzene	µg/kg	<0,1
4-Aminodiphenyle	µg/kg	<0,1
4-Chloroaniline	µg/kg	<0,1
Aniline	µg/kg	<0,1
Benzidine	µg/kg	<0,1
o-Aminoazotoluene	µg/kg	<0,1
4-Chloro-o-toluidine	µg/kg	<0,1
o-Anisidine	µg/kg	<0,1
o-Toluidine	µg/kg	<0,1
2,4 Diaminoanisole	µg/kg	<0,1
p-Toluidine	µg/kg	<0,1

Johannes Wächter
(Food Chemist / Scientific Expert)